Journal Pre-proof

Remediation of soil and water contaminated with petroleum hydrocarbon: A review

Innocent Chukwunonso Ossai, Aziz Ahmed, Auwalu Hassan, Fauziah Shahul Hamid

PII: S2352-1864(18)30364-X
DOI: https://doi.org/10.1016/j.eti.2019.100526
Reference: ETI 100526

To appear in: *Environmental Technology & Innovation*

Received date : 13 August 2018
Revised date : 12 September 2019
Accepted date : 1 November 2019

Please cite this article as: I.C. Ossai, A. Ahmed, A. Hassan et al., Remediation of soil and water contaminated with petroleum hydrocarbon: A review. *Environmental Technology & Innovation* (2019), doi: https://doi.org/10.1016/j.eti.2019.100526.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2019 Published by Elsevier B.V.

Journal Pre-proof

Remediation of soil and water contaminated with petroleum hydrocarbon: A review

Innocent Chukwunonso Ossai[a,b], , Aziz Ahmed[a,b,c], Auwalu Hassan[a,b,d], Fauziah Shahul Hamid*[a,b]

[a]*Institute of Biological Sciences, Faculty of Science, University of Malaya, 50603 Kuala Lumpur*
[b]*Centre for Research in Waste Management, Faculty of Science University of Malaya, 50603 Kuala Lumpur*
[c]*Faculty of Marine Sciences, Lasbela University of Agriculture, Water and Marine Sciences Uthal, Balochistan, Pakistan*
[d]*Department of Biological Sciences, Faculty of Science, Federal University Kashere, Gombe State Nigeria*
Email: fauziahsh@um.edu.my

Abstract

The global use of petroleum hydrocarbons for energy and raw materials in various applications has increased with extensive release of a wide variety of contaminants into the environment, affecting soil, surface water and groundwater. The effect results to numerous health, ecological and environmental issues. However, treatment of contamination and pollution caused by petroleum hydrocarbons is a huge and laborious work. It involves several *in situ* or *ex situ* treatments comprising containment, separation and destruction which include biological, chemical, physico-chemical, thermal and heat, electric and electromagnetic, acoustic and ultrasonic treatment methods. These treatment methods involve several other techniques and strategies as listed in this review. The health risks pose by petroleum hydrocarbon pollution have driven scientists to research, develop and implement risk-based remediation strategies for restoration and reclamation of affected environments. To select the best treatment option for remediation, it is important to comprehend the nature, composition, properties, sources of pollution, type of environment, fate, transport and distribution of the pollutants, mechanism of degradation, interaction and relationships with microorganisms, the intrinsic and extrinsic factors affecting remediation. It helps to evaluate and predict the chemical behaviour of the pollutants with the short and long-term effects and mitigate the effects of pollution and limit exposure to the pollutants. Despite the available remediation options for petroleum hydrocarbon management and removal, sufficient and complete remediation can be implemented by adoption of proper approach derived from risk-based management procedure that can be practical, scientifically defensible, widely adapted, sustainable, non-invasive, eco-friendly and cost-efficient. This paper provides an overview of the various remediation and treatment technologies derived from risk-based approaches that are used for isolation, containment, separation, restoration reclamation and remediation of soil, sediments, surface water and groundwater contaminated by petroleum hydrocarbons and organic compounds.

Keywords: petroleum hydrocarbon, contaminants, pollutants, remediation, biodegradation, bioremediation, pollution.

1. Introduction

The presence of petroleum hydrocarbon contaminants in soil and water environments causes significant environmental impacts and poses a substantial hazard to both human and other forms

of live in the polluted environments (Sammarco et al., 2016; Hentati et al., 2013; Macci et al., 2013). Petroleum hydrocarbon contaminants characterize vast majority of organic compounds and by-products that are classified as priority environmental pollutants such as persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) due to their persistence and recalcitrant nature. They are mostly durable and stable, and thus remain long in the environment and do not undergo degradation easily (Gennadiev et al., 2015; Jesus et al., 2015; Dindar et al., 2013; ATSDR 2011; Keramitsoglou et al., 2003). These contaminants are usually introduced anthropogenically into the ecosystem, resulting to numerous environmental issues, ecological disasters and social catastrophes globally. This phenomenon has awaken the scientific interest in studying the distribution, environmental fate, transport, and chemical properties of the contaminants in the affected environments in order to develop appropriate, cost-effective and environmental friendly strategies that are faster, practical and adjustable in many physical settings for restoration and reclamation of the affected environments (Fallgren & Jin 2008; ATSDR 2011; Costa et al., 2012; Snape et al., 2001; Alexandar, 2000; Sempel et al., 2003; Stroud et al., 2009; US EPA, 1986). Petroleum hydrocarbon characterization is very important in evaluating and predicting the chemical properties and behaviour of contaminants with the short and long-term effects on the affected sites. To understand the scope and the best treatment options for remediation of soil surface water and groundwater contaminated with petroleum hydrocarbon, it is vital to understand the nature, composition and properties of the contaminants, type of environment, fate, transport and distribution of the contaminants in the affected environment, mechanism of contaminants degradation, the interactions and relationships with microorganisms and the intrinsic and extrinsic factors affecting degradation of the pollutants, in order to predict and mitigate effects of pollution and to limit exposure of human and animals to the contaminants (Artiola et al., 2004; Valentin et al., 2013).

2. Sources of petroleum hydrocarbon pollution

Sources of petroleum hydrocarbon entering the environment are numerous as the number of individual hydrocarbon components are quite large. The inadvertent or deliberate and uncontrolled anthropogenic release of petroleum hydrocarbon pollutants resulting from oil and gas exploration and production, transportation and storage, tank leakages, accidental spills in loading and discharging, ballasting and de-ballasting, bunkering, oil tanker incident, petrochemical industry effluent discharge, fugitive emissions, burst in aged underground pipelines, war and political crisis, sabotage, and natural disasters perturb the environment to leave negative impacts in the terrestrial and marine environments, posing direct and indirect health risk to all forms of life in the affected environment through alteration of population dynamics and disruption of trophic interaction and natural community structure within the ecosystem (Sajna et al., 2015; Souza et al., 2014; Bejarano and Michel, 2010; Deppe et al., 2005; Margesin and Schineer, 2001; Belousova et al. 2001).

In the soil, petroleum hydrocarbons can affect the soil physical properties, such as soil texture, compaction, structural status, penetration resistance, saturated hydraulic conductivity and the soil chemical properties such as mineral and heavy metal concentration and content (Hreniuc et al., 2015). The causes of pollution can be numerous, but the impacts, effects and consequences are the same. Seepage from natural oil deposits from deep inland and offshore explorations is among the major routes through which petroleum hydrocarbon pollutants enter soil and marine environments where the latter serves as the largest reservoir and ultimate receiver of pollutants

(Varjani, 2017; Ron and Rosenberg, 2014; Atlas, 1981). The EPA Toxic Release Inventory report (2005) stated that crude oil industry is among the major sources releasing petroleum hydrocarbon contaminants into the environment. It was estimated that about 1.7-8.8 million metric tonnes of petroleum hydrocarbon is being released annually into the marine environment globally with 90% attributed to accidents due to human failures and release from oil tanker incidents at sea (Dadrasnia, et al., 2013; Zhu et al., 2001). The National Research Council of the U.S. National Academy of Science (NRC) 2002 reported that 8.4 million tonnes are lost to the ocean waters per year while the main sources contributing to the total input was recorded as follows: natural seeps account for 46%, land-based sources recorded 37%, accidental spills recorded 12% and oil extraction recorded 3%. The oil tanker spill statistics (2016), reported 6 million metric tonnes of petroleum hydrocarbon has been lost to the marine environment from 1970-2016, while natural petroleum oil leakage was recorded at 600,000 metric tonnes per year (Kvenvolden and Cooper, 2003). Despite the overall number of the total input in ocean waters, major accidental oil tanker spills still occur at irregular intervals. The spills account for about 10-15 percent of all oil spill that is lost annually to ocean waters worldwide (Clark, 1999).

3. Nature and composition of petroleum hydrocarbons

Petroleum hydrocarbons naturally occur in deposit, in the subterranean, beneath the earth surface in the sedimentary rocks, existing in the form of gases (natural gas), semisolids (bitumen), solids (wax or asphaltite) and liquids, as petroleum crude oil commonly known as fossil fuel comprising simple to complex mixture of various hydrocarbon compounds in form of aliphatic saturated compounds or paraffins including straight and branched chain alkanes (n-alkanes), cycloalkanes, unsaturated alkenes, alkynes; aromatics including polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, monoaromatic such as benzene, toluene, ethylbenzene, xylene (BTEX); asphaltenes including phenols, fatty acids, ketones, esters, porphyrins; resins including pyridines, quinolines, cardaxoles, sulphonates, amides; as well as waxes and tars as shown in Table 1 (Varjani, 2017; Moubasher et al., 2015; Speight, 2014; Riazi, 2005). The non-hydrocarbon components of petroleum oil consist of sulphur compounds such as sulphides, thiols, cyclic sulphides, disulphides, dibenzothiophene, benzothiophene, and naphthobenzothiophene; oxygen compounds include alcohols, carboxylic acids, esters, ethers, ketones and furans; and nitrogen compounds include pyrrole, pyridine, indole, benzo(a)carbazole, carbazole, benzo(f)quinolone, nitriles, indoline, and quinoline, (Speight, 2007). Certain metals can also be found, and these hetero-compounds are mostly contained in the non-volatile component of the petroleum hydrocarbons (Speight, 2001; Speight, 2007; Costa et al., 2012).

4. Environmental fate and transport of petroleum hydrocarbons

When petroleum hydrocarbons enter the environment, the components undergo a variety of processes such as physical abiotic processes, chemical, and biological changes through interaction with microorganisms and metabolic pathways collectively known as weathering (Abdel-Shafy and Mansour, 2016). The level at which various components of the petroleum hydrocarbon deteriorates under weathering processes depends largely on the nature, composition, physical and chemical characteristics of the hydrocarbons. The weathering process includes adsorption to soil particles and organic materials, volatilization to the atmosphere, and dissolution in water (Esbaugh et al., 2016; Mishra and Kumar 2015; Barakat et al., 2001). The

aliphatic hydrocarbons are more inclined to be volatile than aromatics hydrocarbons because of the molecular nature. If volatilization is the main weathering process, the loss of lower molecular weight aliphatic hydrocarbons will be the most dominant change in the petroleum hydrocarbon, which may be the principal air pollutants causing air pollution at the contaminated site (Maletic et al., 2013; Peter, 2011).

In water environment, petroleum hydrocarbons tend to float on the surface and form thin surface films or slicks and its weathering process includes spreading, evaporation, dissolution, dispersion and emulsification, while the higher molecular fractions sink to the bottom of the water (Mishra and Kumar 2015). Under certain marine conditions, petroleum hydrocarbons and sea water may form an emulsion, a viscous substance called "mousse" (Rodriques and Totola, 2015). Erosion of coastal sediments redistributes petroleum hydrocarbons into water column allowing for transport and exposure to marine lives. The mechanism is affected by environmental factors such as wind flow velocity, atmospheric pressure, temperature, turbulent flow and surface characteristics (Al-Majed et al., 2012). Among the significant weathering processes, evaporation is the most immediate and rapid and has the most effect on the mass of the contaminants (Lee et al., 2015).

On terrestrial environment, petroleum hydrocarbons permeate vertically downward through the unsaturated oil until they reach the groundwater and spread sidewise or laterally (Banerji 1995). The distribution of contaminants may be present in four different forms, some are dissolved in water, some are sorbed on solid organic particles, some formed the soil gas and non-aqueous phase liquid commonly known as NAPL and the components segregate from the mix based on their physicochemical parameters (Logeshwaran et al., 2018). The fastest physical abiotic weathering process involves evaporation of lower molecular weight aliphatic hydrocarbons while physical, chemical and biological processes involve spreading, dispersion, evaporation, dissolution, sinking, emulsification, foamy mousse formation, photo-oxidation, resurfacing, tarball formation and biodegradation (Souza et al., 2014). Many petroleum hydrocarbons have a high affinity for organic matter and can easily adsorb to organic materials and attach to soil and sediment due to their hydrophobicity (Clay, 2014).

5. Toxicity effect from petroleum hydrocarbon exposure

With the immense number of compounds contained in petroleum hydrocarbons, only a little fraction of the compounds is well characterized for toxicological effect (ATSDR 2011). Petroleum hydrocarbon compounds with wide range of relative molecular mass and boiling points caused various degree of toxicity to the affected environment. The toxic effects of the compounds and bioavailability to substrates depend largely upon their chemical composition and physical state (Van der Hauel, 2009). Petroleum hydrocarbons are usually toxic and lethal depending on the chemical nature, composition and properties of the compound fractions, mode of exposure, level of exposure and time of exposure. The contaminants can cause various range of toxicological health problems to humans and animals including haemotoxicity (destruction of red blood cells), carcinogenicity (ability or tendency to induce cancer), genotoxicity (ability to induce non-transmissible DNA damage), mutagenicity (capacity to incite transmissible genetic mutations), teratogenicity (induction of malformation of embryo or foetus), cytotoxicity (ability of being toxic to cells), neurotoxicity (damage to the brain and nervous system), immunotoxicity (capacity to repress the immune system), nephrotoxicity (damage to the kidney), hepatotoxicity (ability to elicit damage to the liver), cardiotoxicity (capacity to cause damage to heart muscles) and ocular toxicity (ability to induce eye disorders) (Lawal, 2017; Gutzkow, 2015; Azeez et al.,

2015; Ogunneye et al., 2014; Zheng et al., 2014; Sriram et al., 2011; Omoti et al., 2008; Cajaraville et al., 1991, WHO, 1986). It also has inhibitory growth effects on plants when they obstruct or lower the water and mineral salt intake which cause breakdown of plants metabolic processes resulting into deficiency of chlorophyll and nutrients that lead to the decline in resistance to pest and diseases, exhibit stunted growth, deformed roots, leaves and flowers with chlorosis and necroses (Rusin et al., 2015; Shan et al., 2014; Zhu, 2010; Méndez-Natera et al., 2004; Adam and Duncan, 2002; Vavrek and Campbell, 2002;). Figure 1 shows some toxicological short and long-term health effects of overexposure to petroleum hydrocarbons.

6. Mechanism of degradation for petroleum hydrocarbon

Petroleum hydrocarbon degradation is the result of combined effects of chemical transformation and biodegradation (Joutey et al., 2013). The degradation of petroleum hydrocarbons is a complex process that relies on the nature, composition and the concentration of hydrocarbons present in the impacted medium. It comprises series of steps involving chemical transformation and mineralization of contaminants, through metabolic and enzymatic activities which change into less harmful and non-hazardous substances that are assimilated into the biogeochemical cycles (Abbasian et al., 2015; Maletic et al., 2013). Petroleum hydrocarbons are mostly degraded by enzyme-specific biodegradation mechanisms involving aerobic (in presence of oxygen) or anaerobic (in absence of oxygen), attachment and binding of microbial cells to the substrates with the production of biosurfactants and emulsifiers (Varjani and Upasani, 2016; Das and Chandran, 2010). Light can also degrade petroleum hydrocarbon contaminants while many volatile components are desorbed or evaporate shortly after pollution occurs (Van der Heul, 2009). Photolytic splitting is initiated by the association with light. During absorption of photon energy, the components of the petroleum hydrocarbon such as the simple aromatic compounds benzene, toluene, ethylbenzene, xylene (BTEX) and polycyclic aromatic hydrocarbons (PAHs) reach their photo-excited states that facilitate their disintegration leading to the degradation of light absorbing compounds within the mixture (Logeshwaran et al., 2018). Dissolution occur based on the solubility of the components. The solubility varies based on the specific properties such as molecular size, structure and polarity (Clay, 2014). Electromagnetics and ultrasound energy can stimulate mechanisms such as volatilization, seepage, desorption, airflow and microbial activities (Kuppusamy et al., 2016a; Kuppusamy et al., 2016b). As depicted in Figure 2, most of the degradation of petroleum hydrocarbon contaminants is initiated under chemotrophic aerobic condition where the initial intracellular activity is an oxidative reaction catalysed by enzymes such as oxygenases and peroxidases and the degradation pathways convert petroleum hydrocarbon contaminants into intermediates (Fritsche and Hofrichter, 2000).

7 Chemical processes in petroleum hydrocarbon degradation

The chemical processes involve in degradation of petroleum hydrocarbons are biotic and abiotic chemical transformations and mineralization (Aeppli et al., 2014). The abiotic chemical transformation involves reactions not initiated by microorganisms that decrease contaminant concentrations by degrading the chemicals into simpler or other products by hydrolysis and oxidation reduction (Maletic et al., 2011; Peixito et al., 2011; Brasington et al., 2007; Stroud et al., 2007). In water, hydrolysis is catalysed by H_3O^+, H^+ or OH-, but in soil, loosely complexed metal ions are important catalysts for chemical reactions. The biotic chemical transformation involves biodegradation and biotransformation.

Chemical processes involve the combined effects of chemical transformation and biodegradation. It can occur under anaerobic and aerobic conditions. Degradation inclines to increase in the following order: asphaltenes < PAHs < cyclic alkanes < monoaromatics < low molecular weight n-alkyl aromatics < branched alkenes < branched chain alkanes < n-alkanes (Atlas, 1981; Van Hamme et al., 2003; Tyagi et al., 2011). In the presence of oxygen (O_2) degradation can be activated by enzymes (oxygenases) and completely oxidized to carbon dioxide (CO_2) and water (H_2O) as shown in Figure 3.

8. Remediation of contaminants in soil and water environments

It is widely acknowledged that petroleum hydrocarbon pollution in the soil, sediments, surface water and groundwater poses a huge threat to human health. The remediation treatment methods and techniques play a vital role in complete cleaning, containment, removal, reclamation and restoration of contaminated environment. Remediation approach chosen for any contaminated environment is site specific, and the variables associated with the nature and composition of the pollutants, the physical, chemical and biological conditions of the affected environment together with the microbial community present or required augmentation are considered. In addition, the mechanisms, the regulatory requirements, the cost and time constraints are considered in the selection of any suitable remediation treatment technique. However, in response to the increasing demand to respond to environmental pollutions, the primary focus of environment scientists now relies on the adoption of a risk-based management approaches to remediate contaminated environments as shown in Figure 4 as a response to the health risks or control of the damaging effects on the affected environment. In most cases, authorities focus their remediation priorities particularly on the most urgent cases with less difficulty to remediation. The impacted environments are mostly soils, surface water, sediments and groundwater which are usually contaminated with high and low molecular weight petroleum hydrocarbon compounds, volatile organic compounds (VOCs), semi volatile organic compounds (SVOCs), polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs), hydrophobic organic compounds (HOCs), non-aqueous phase liquids (NAPL), xenobiotic organics and heavy metals. These contaminants can spread or migrate to the environment far from the original location and threatens fauna and flora communities in the impacted area. The remediation options adopted by pollution experts serve as a means of managing the contaminated environments (Thavamani et al., 2015). The management system leads to the selection of remediation approach from containment, separation and destruction methods based on several *in-situ* and *ex-situ* remediation treatment technologies for soil, surface water and groundwater comprising biological, chemical, physicochemical, thermal, electric, electromagnetic and ultrasonic treatment methods (Reddy, 2013; Rodrigo et al., 2014; Chang et al., 2016; Saksa, 2017). These remediation techniques can contain, sequester, separate, extract, remove, destroy, transform and mineralize contaminants in the polluted environment into less harmful, non-hazardous and less reactive forms (Maletic et al., 2013). Remediation in water environment includes remediation of surface water and groundwater contaminated by pollutants, whereas soil remediation includes remediation of topsoil, subsoil and sediment contaminated by pollutants. Depending on the extent of the contamination and pollution, soil and water remediation may be conducted separately or together. The success of any treatment approach on any given contaminated site or environment depends on the design, adjustment of the system operations based upon the properties of the contaminants, the soil and the performance of the systems. Integration of one remediation approach with another approach either simultaneously or

sequentially may result in a synergistic or combined effect among the treatment approach deployed (Riser-Roberts, 1998). The next section will discuss the various restoration and remediation treatment methods for soil, sediments, surface water and groundwater contaminated with petroleum hydrocarbon compounds and many other organic compounds.

9. Biological treatment methods

The feasibility of a biological treatment method depends largely on the limiting factors as well as the location of the contaminants. It also depends on the contaminated soil, sediments, surface water and groundwater to be remediated, whether it is intact in the environment or to be removed, excavated and transported for treatment to an offsite treatment facility. If treatment is on site, the term *in-situ* suffices and if treatment is offsite, *ex-situ* suffices (Hamzah et al., 2013). Biological remediation methods have shown remarkable success for *in situ* and *ex situ* remediation. They are capable of remediating or degrading petroleum hydrocarbons and various organic contaminants to simpler and non-toxic substances without any long-term adverse effect on the impacted environments (Lim et at., 2016). The biological remediation methods require long treatment period ranging from months to several years in order to achieve a satisfactory and effective removal of contaminants while high concentration of contaminants may result into low microbial activity with low or insufficient removal efficiency (Margesin et al., 2007).

9.1 Bioremediation (*in-situ and ex-situ*)

This is facile, environmental-friendly, sustainable, and cost-efficient method for restoration and cleaning of contaminants in the soil. It involves the natural degradation of petroleum hydrocarbon contaminants by hydrocarbon degrading microorganisms such as bacteria, fungi and yeast. It removes and neutralises contaminants in the soil into non-toxic or simpler compounds such as carbon (IV) oxide and water through oxidation under aerobic condition by the microorganisms with nutrient supply and optimization of the limiting factors for their biological activities (Yanti, 2018; Dzionek et al., 2016; Kostka et al., 2011; Wu et al., 2007;). Before adopting to bioremediation, it is important to evaluate all the limiting parameters that can effectively affect the efficacy of the remediation process. The aliphatic hydrocarbons are more easily degradable by the microorganisms whereas the long chain and the branched or cyclic chain hydrocarbon are more resistant to bioremediation (Maletic et al., 2011). The hydrocarbon degrading microorganisms utilize carbon compound as source of energy, growth and reproduction. Bioremediation using selected microorganisms for petroleum hydrocarbon degradation is increasing the interest of researchers. Some of the most commonly isolated petroleum hydrocarbon degrading bacteria belong to the genus *Pseudomonas* which efficiently degrade petroleum hydrocarbon into simpler compounds (Wang et al., 2011; Wongsa et al., 2004). In addition, fungi species such as *Penicillium*, *Fusarium*, and *Rhizopus* species have been isolated and utilized in bioremediation of petroleum hydrocarbon contaminated soil and sediments (Mancera-López et al., 2008; Potin et al., 2004). However, bioremediation of petroleum hydrocarbon has been in use since 1940 but gained popularity after the Exxon Valdez spill in 1980 (Hoff, 1993).

9.2 Bioattenuation (*in-situ and ex-situ*)

This is the use of naturally occurring processes including a variety of physical and biochemical processes to remove, transform, neutralize and reduce the mass, volume,

concentration and toxicity of the contaminant. The process occurs through advection, dispersion, sorption, dissolution, volatilization, chemical transformation, abiotic and biological transformation, stabilization and biodegradation to manage contaminant from a residual source (Abatenh et al., 2017; Vasquez et al., 2017; Agarry and Latinwo, 2015). Bioattenuation is applicable for contaminated sites with low concentration of contaminants, where other remediation methods cannot be adopted (Vásquez-Murrieta et al., 2016).

9.3 **Biostimulation *(in-situ and ex-situ)***

This is an addition of any stimulatory materials, bulking agents, nutrients amendments, bio-surfactants, biopolymers and slow release fertilizers to enhance and support microbial growth and enzymatic activities of the autochthonous microorganisms in the contaminated soil for remediation activities (Wu et al., 2016; Lim et al., 2016; Adams et al., 2015; Agarry and Latinwo, 2015). Biostimulation is achieved by addition or optimization of various forms of limiting parameters, micronutrients and electron acceptors such as nitrogen, phosphorus, potassium, carbon and oxygen, which are mostly available in low concentrations in the contaminated soil and it lowers or constrains the microbial performance. The problem associated with chemical nutrient addition to contaminated soil and groundwater is different from microbial addition (Hazen, 2010). Biostimulation is the most successful and efficient bioremediation method in comparison with other *in situ* remediation in simulated soil contaminated with petroleum hydrocarbons (Simpanen et al., 2016). The biostimulation requirements include presence of correct microorganisms, ability to stimulate target microorganisms, ability to deliver nutrients, C:N:P-30:5:1 for balance growth (Hazen, 2010). Singh et al. (2012) investigated biodegradation of petroleum hydrocarbon contaminated soil over a period of 18 months using bacterial consortium and nutrient mixture to achieve removal efficiency of 99.9%.

9.4 **Bioaugmentation *(in situ and ex situ)***

This involves the addition of exogenous microbial cultures, autochthonous microbial communities or genetically engineered microbes with specific catabolic activity which have adapted and proven to degrade contaminants to enhance degradation or increase the rate of degradation (Nwankwegu and Onwosi, 2017; Poi et al., 2017; Kastner and Miltner, 2016; Nzila et al., 2016; Abdulsalam et al., 2011). In the oil polluted site of ONGC field in Gujarat, India, Virjani et al. (2015) demonstrated *in situ* bioaugmentation using hydrocarbon utilizing bacteria consortium comprising six bacterial isolates for degradation of petroleum hydrocarbon contaminants and achieved removal efficiency of 83.7% over a period of 75 days. Corvino et al. (2015) also demonstrated bioaugmentation by using autochthonous fungi from a petroleum hydrocarbon contaminated soil to degrade clay soil contaminated with petroleum hydrocarbons and achieve removal efficiency of 79.7% after 60 days period.

9.5 **Bioventing *(in situ)***

This is injection of air (oxygen) into the contaminated soil in order to increase the *in situ* degradation and to minimize volatile contaminants to the atmosphere (Trulli et al., 2016; Camenzuli and Freidman, 2015; Inturbe and López, 2015). The addition of air to the soil

stimulates and increases aerobic condition for the growth of indigenous microorganisms and enhances the catabolic activity of the contaminants. Bioventing has been used for remediation of petroleum hydrocarbon contaminated soil. In a study demonstrated by Agarry and Latinwo (2015), bioventing was conducted on diesel oil contaminated soil amended with brewery effluents as organic agent over 28 days period and achieved a removal efficiency of 91.5%. Thomé et al. (2015) also demonstrated a similar assessment for remediation of diesel-contaminated soil without any soil amendment and obtained removal efficiency of 85% after 60 days period.

9.6 **Biosparging *(in situ)***

This involves injection of air (oxygen) and nutrient into the saturated zone under pressure to increase groundwater oxygen concentration to stimulate biological activities of the indigenous microorganisms to degrade contaminants (Azubuike et al., 2016; Singh and Garima 2015; Coste et al., 2013). Biosparging is used to reduce the contaminant concentration adsorbed to soil, and within the capillary fringe above the water table, as well as contaminants dissolved in the groundwater. The effectiveness of biosparging depends on soil permeability and pollutant degradability (Philip and Atlas, 2005). Kao et al. (2007) demonstrated biosparging at a petroleum oil spill site, and obtained 70% removal efficiency for BTEX within 10 months remedial period. The limitation of biosparging is in the predicting the direction of airflow in the process as it depends on the high airflow rate in order to achieve pollutant volatilization and promote degradation.

9.7 **Bioslurry *(ex situ)***

This involves treatment of contaminated soil in a controlled bioreactors such as sequencing batch, feed-batch, continuous and multistage bioreactors (Megharaj and Naidu, 2017; Zappi et al., 2017; Azubuike et al., 2016). In the treatment process, nutrients are added to enhance microbial activities to degrade the contaminants. The reactor is designed with various process controls to enable monitoring, control and manipulation of temperature, mixing and addition of nutrients to achieve maximum removal efficiency. Other advantages include faster reaction kinetics, better control of emissions and little space requirement. The limitations include longer treatment time, soil excavation and transportation to the treatment facility, pretreatment is sometime required, required materials that easily dispersed in water and required control of volatile emissions (Banerji 1995). In a recent study demonstrated by Tuhuloula et al. (2015), who conducted bioslurry of petroleum hydrocarbon contaminated soil obtained from oil drilling site of Pertamina Petrochina in Indonessia with microbial consortia of *Bacillus cereus* and *Pseudomonas putida* and obtained naphthalene removal efficiency of between 79.35 – 99.73% after 49 days in a slurry bioreactor.

9.8 **Biopiling *(ex situ)***

This involves combination of landfarming and composting in an engineered cell aerated with blowers and vacuum pumps, irrigation and nutrient system as well as leachate collection system for bioremediation of pollutant components adsorbed to soil and sediments (Kim et al., 2018; Benyahia and Embaby, 2016; Wu and Coulon, 2015). The technique involves piling of an excavated contaminated soil, followed with biostimulation and aeration to enhance microbial activities for degradation. It is suitable

for treatment of large volume of contaminated soil and sediments in a limited space and effectively remedy pollutions in extreme environments (Whelan et al., 2015). The basic components of the technique includes addition of air (oxygen), moisture (water), nutrients and bulking agents (organic materials), leachate collection system and treatment bed. Biopiling of contaminated soil can limit volatilization of low molecular weight contaminants in petroleum hydrocarbons (Dias et al., 2015). In a study demonstrated by Gomez and Sartaj (2014), who conducted biopiling treatment of petroleum hydrocarbon contaminated soil in a field scale at low temperature using a consortia of microorganisms and organic compost for a period of 94 days. The result obtained showed a removal efficiency of 90.7% for total petroleum hydrocarbon (TPH).

9.9 **Biotransformation** ***(in situ and ex situ)***

Biotransformation is a biotechnological process that involves structural modifications in the chemical components, aided by microorganisms or enzyme systems to form molecules with high polarity (Smitha et al., 2017). This process transforms organic compounds from one form to another in order to reduce its toxicity and persistence of the contaminants (Jing et al., 2016; Størdal et al., 2015). Although natural biotransformation process occur very slowly, it is nonspecific and less productive but microbial biotransformation or microbial biotechnology generate metabolites in high amount, more rapid and productive, with more specificity. Microbial biotransformation is used in the remediation of various contaminants and large variety of compounds including petroleum hydrocarbons. The biotransformation can occur in oxidation, reduction, condensations, isomerization, hydrolysis, denitrification, sulfidogenesis, methanogensis, introduction of functional group and formation of new bonds (Karthikeyan and Bhandari, 2001). Biotransformation of petroleum hydrocarbon contaminated soil can take place in the presence of bacteria, yeast and fungi (Atlas, 1981). However, genetically modified organisms (GMOs) or genetically engineered microorganisms (GEMs) have shown potential in biotransformation of contaminants in soil (Abatenh et al., 2017). In a study demonstrated by Al-Bashir et al. (1990), who conducted biotransformation of naphthalene at the concentration of 50 mg/L in a slurry system under denitrifying conditions for 50 days period. The results obtained showed about 90% of the total naphthalene was transformed at a maximum mineralization rate of 1.3 mg/L per day.

9.10 **Landfarming** ***(in situ and ex situ)***

This is an engineered bioremediation system, which employs tilling, ploughing and spreading of the impacted soil in a thin layer on the land surface to enhance and stimulate aerobic microbial activities with addition of nutrients. It is suitable for treatment of soil contaminated with low molecular weight petroleum hydrocarbons, volatile organic compounds (VOCs) and variety of other organic compounds (Guarino et al., 2017; Brown et al., 2017, Wang et al., 2016). Enhancing the biodegradation in landfarming is achieved by addition of oxygen, moisture and nutrients. Tilling also introduces oxygen to the soil and helps to increase evaporation while addition of nutrients or soil amendments such as organic fertilizers provide nutrients to stimulate the microbial activities. In a study demonstrated by Brown et al. (2017), who conducted landfarming to improve bioremediation of petroleum hydrocarbons in the soil for a period of 110 days with nutrient addition. The results obtained after 6 weeks showed 53% for total petroleum

hydrocarbon (TPH) removal from the contaminated soil. This indicated that landfarming is a successful treatment option for remediation petroleum hydrocarbon contaminated soil. In a similar research demonstrated by Guarino et al. (2017), who conducted bioremediation assessment on petroleum hydrocarbon contaminated soil, using natural attenuation, landfarming and bioaugmentation-assisted landfarming for 90 days period. The results obtained showed that bioaugmentation assisted landfarming produced the best result reaching a reduction of 86% for the total petroleum hydrocarbon and this was followed by landfarming with 70% reduction and natural attenuation with 57% reduction.

9.11 **Composting *(in situ and ex situ)***

This is a controlled microbial aerobic biochemical degradation of organic waste materials and its conversion into a stabilized organic material that can be used as soil conditioners for remediation of soil contaminated with organic compounds (Ren et al., 2018; Saum et al., 2018; Cai et al., 2017). The composting process involves careful control with nutrient addition, tilling, watering and addition of suitable microbial consortia as well as bulking materials in form of organic waste to improve bioremediation (Prakash et al., 2015). Compositing requires thermophilic conditions of 50-65ºC to properly compost soil contaminated with hazardous compounds such as petroleum hydrocarbon compounds. An increased temperature resulted from heat generated from the microbial activities during the breakdown of organic materials in the compost. Sufficient degradation is achieved through periodic tilling, watering and aeration. In a study demonstrated by Atagana (2008), who conducted bioremediation of petroleum hydrocarbons using sewage sludge compost for a period of 19 months on contaminated soil with concentration of 380,000 mg kg^{-1} for total petroleum hydrocarbon (TPH). The results obtained after the experiment period showed 99% reduction in the total petroleum hydrocarbon (TPH), while other selected hydrocarbon components where reduced 100% within the experiment period. Therefore, composting helps to degrade, convert and bind contaminants into harmless substances and compounds with substantial potential for remediation application for treatment of contaminated soil (Prakash et al., 2015).

9.12 **Windrows *(ex situ)***

This relies on periodic tilling and turning of piled contaminated soil with addition of water to bring about increased aeration and distribution of nutrients to enhance biodegradation. The increase in microbial activities by the autochthonous and transient hydrocarbonoclastic microbes that exist in the contaminated soil speed up the rate of biodegradation and this is accomplished by biotransformation, assimilation and mineralization (Azubuike et al., 2016; Jiang et al., 2016; Coulon et al., 2010). This treatment method when compared with biopiling showed more higher rate of hydrocarbon removal efficiency. On the downside, windrow treatment is not the best option in remediating soil contaminated with volatile compounds due to the release of toxic volatile compound during the periodic turning and tilling (Azubuike et al., 2016). There is emission of greenhouse gases such as methane (CH_4) in windrow treatment due to the formation of anaerobic zone within the piled heap (Hobson et al., 2005). In a study demonstrated by Al-Daher and Al-Awadhi (1998), who conducted bioremediation of petroleum contaminated soil using windrow soil system for a period of ten months. The windrow system was subjected to regular watering, tilling and turning to enhance

aeration and microbial activities. The results obtained showed 60% reduction in the total petroleum hydrocarbons in the first eight months and the degradation rate can also be enhanced if the moisture content is controlled effectively.

9.13 **Vermicomposting or Vermiremediation *(in situ and ex situ)***

This is the utilization of earthworms to clean up contamination from polluted soil (Njoku et al., 2017; Chachina et al., 2016; Ekperusi and Aigbodion, 2015). The presence of earthworms in the soil enhances and improves soil fertility, biological, chemical and physical properties of the soil. Earthworms stimulate and enhance microbial activities through creating suitable conditions for microbes to thrive and improve soil aeration by burrowing and tunneling through the soil structure (Dabke, 2013). The presence of earthworms in the soil depends on soil moisture, organic matter content and pH. Earthworms mostly occur in diverse habitats, especially those habitats reach in organic matter and moist. Vermiremediation of petroleum hydrocarbon occurs through degradation (vermidegradation) and the earthworms stimulate the bioremediation by enhancing the oxidation process, aeration of soil and enhancing the microbial actions which increases the microbial availability to the petroleum hydrocarbon components (Schaefer and Juliane, 2007). In a study demonstrated by Azizi et al. (2013), who conducted vermiremediation using earthworm (*Lumbricus rubellus*) to degrade petroleum hydrocarbon components such as polycyclic aromatic hydrocarbons (PAHs), anthracene, phenanthrene and benzo(a)pyrene (BaP) within period of 30 days. The result obtained showed removal efficiency of 99.9% for PAHs. In a similar studies demonstrated by Sinha et al. (2008), who conducted the remedial action of earthworms on polycyclic aromatic hydrocarbons (PAHs) contaminated soils from a gasworks site. The result obtained showed 80% removal efficiency for PAHs as compared to 21% removal efficiency in microbial degradation only.

9.14 **Trichoremediation *(in situ and ex situ)***

This is the use of the enzymatic actions of keratinolytic and keratinophilic bacteria and fungi found on the keratinous materials such as hairs and feathers containing keratins to remediate soil contaminated with petroleum hydrocarbons. In a study demonstrated by Ulfig et al. (2003), who investigated bioremediation progress in contaminated soil obtained from a petroleum refinery and using keratinolytic fungi as indicators for petroleum hydrocarbon contamination. The occurrence of keratinolytic fungi in the biopile indicated the presence of human hairs, feathers or animal hairs, which formed keratinous debris to the soil. The keratinous debris is the main substrate for growth of soil keratinolytic microbes (Garg et al., 1985). In the study, sensitivity to petroleum hydrocarbon by keratinolytic fungi was investigated, and the fungi isolates were able to remove petroleum hydrocarbons from the medium during degradation of keratin proteins. This is a good indication that keratinous materials can be utilized for trichoremediation of petroleum hydrocarbon contaminated soil.

9.15 **Mycoremediation, mycodegradation *(in situ and ex situ)***

This involves the use of fungi processes to degrade contaminants to less toxic or non-toxic forms, thereby reducing or eliminating environmental contaminants (Kumar et al., 2018; Ali et al., 2017; Anderson and Juday, 2016). Fungi have the capability to degrade

variable environmental recalcitrant pollutants due to their ability to produce and secrete extracellular enzymes such as peroxidases that can break down the lignin and cellulose (Jang et al., 2009; Rajput et al., 2011). Ligninolytic fungi such as the white rot fungi *Polyporus sp*. and *Phanaerochaete chrysosporium* are very important in bioremediation because of their ability to degrade a diverse range of toxic pollutants (Bhatnagar and Kumari, 2013). The degradative action of fungi are recognized in various situation where they degrade different types of materials. Polyethylene has been degraded by the cultivation with *Penicillium sp.* (Yamada-Onodera et al., 2001). Studies have shown that many filamentous fungi species are hydrocarbonoclastic in nature. Some white rot fungi use their mycelia to degrade hydrocarbons due to their high production of oxidative enzymes, extracellular enzymes, chelators and organic acids which help them to degrade petroleum hydrocarbons. In a study demonstrated by Ulfig et al. (2013), keratinolytic fungi *Trichophyton ajelloi* was able to remove hexadecane and pristine from crude oil. In a similar study demonstrated by Njoku et al. (2016), mycoremediation was conducted using fungi *Pleurotos pulmonarius* to remediate soil contaminated with petroleum hydrocarbon mixture comprising petrol, diesel, spent engine oil and spent diesel engine oil at the ratio of 1:1:1:1 in various concentrations of 2.5%, 5%, 10% and 20%. The results obtained after 62 days of incubation showed that the soil with 10% concentration was able to remove 68.34% of total petroleum hydrocarbons while least removal was obtained in the soil with 2.5% treatment concentration with 22.12% removal. These results suggest that the fungi *Pleurotos pulmonarius* has the capability to remediate soil contaminated with moderate level of petroleum hydrocarbon mixture

9.16 **Phycoremediation *(in situ and ex situ)***

This is the use of algal species (macroalgae or microcalgae) to sequester, remove, breakdown, biotransform or metabolize pollutants from contaminated water environment (Phang et al., 2015; Gani et al., 2015; Kushwaha et al., 2014). Algae are capable of accumulating and degrading toxic pollutants and organic compounds such as petroleum hydrocarbons, biphenyls, pesticides and phenolics (Kumar et al., 2008). Algae are known to be very adaptive and can grow in autotrophic, mixotrophic or heterotrophic conditions in most environment. In nature, algae play a vital role in regulating and controlling the concentration of metals in the water environment. The mixotrophic algae are excellent agents for bioremediation and sequestration of carbon (Subashchabdrabose et al., 2013). Algae can produce O_2, and can fix CO_2 by photosynthetic process and increase the BOD level in the polluted water and remove excess nutrients (Fathi et al., 2013). The mineral uptake by microalgae occur in two steps. The initial step is independent of cell processes and involves physical adsorption onto the surface of the cell and the ions are gradually carried into the cell by chemisorption (Bhatnagar and Kumari, 2013). The second step is dependent on cell processes and involves intracellular uptake and absorption. Studies have shown that heavy metals can be sequestered in the polyphosphate body of algae and serves for detoxification and storage (Dwivedi 2012). A number of algae species such as *Chlamydomonas*, *Chlorella*, *Botryococcus* and *Phormidium* have been used in phycoremediation. The use of microalgae in phycoremediation of petroleum hydrocarbon is gaining interest as some algae species can degrade and oxidize petroleum hydrocarbon components into less noxious compounds (He et al., 2013; El-Sheekh et al., 2013). In a study demonstrated by Kalhor et al. (2017), who investigated the potential of

Chlorella vulgaris in phycoremediation of crude oil contaminated water environment. In the study, different crude oil concentrations were treated and the removal efficiency was calculated after 14 days period. The result obtained after the incubation period proved that aromatic compounds (benzene and naphthalene) and the alkane (nonadecane) were remediated at the removal efficiency of 89.17% at 10 g/l and 76.53% at 20 g/l concentration by the algae. Therefore, the investigation confirmed that the algae *Chlorella vulgaris* can remove light components of petroleum hydrocarbon compounds.

9.17 **Phytoremediation *(in situ and ex situ)***

This is the process by which green plants are used to remove or extract contaminants in the soil, sediments, surface water and groundwater. The technique removes the contaminants from the soil (decontamination) or sequesters the contaminants into the matrix (stabilization) (Adam, 2001). The process takes advantage of the natural processes of the green plants (Ossai et al., 2014). The use of plants based systems to remediate environments contaminated with heavy metals, organic and inorganic compounds forms the basis of the reed beds and constructed wetlands (Adam, 2001). Plants can breakdown, degrade, concentrate, sequester, bioaccumulate, contain, stabilize and metabolise contaminants by acting as filters or traps in the tissue through various mechanisms such as phytoextraction (phytoaccumulation), phytodegradation, phytostabilisation, phytotransformation, phytovolatilsation, rhizofiltration, rhizodegradation (rhizoremediation). These mechanisms convert the contaminants into less toxic and less persistent in the environments (Cristaldi et al., 2018; Hussain et al., 2018; Gouda et al., 2016; Kösesakal et al., 2015). The mechanisms and efficiency of phytoremediation depends on the pollutants, bioavailability and properties of the polluted soil. Each of the mechanisms has an effect on the mobility, toxicity of pollutants and volume or concentration of the pollutants. Phytoremediation system uses the synergistic relationship among the plants, microorganisms dwelling in the soil and on the roots of the plants. The plants produce inherent enzymatic actions and uptake processes that remove, sequester and the contaminants. They act as symbiotic host to aerobic and anaerobic microorganisms, providing them with nutrients and habitat. The plants roots and shoots provide colonisable surface area for absorption, exudates and leachates in the rhizosphere for microbial activities (Ahalya and Ramachandra 2006). The success of phytoremediation depends largely on the plant's ability to bioassimilate or bioaccumulate both organic and inorganic contaminants into their cell wall structures and carry out oxidative degradation of organic xenobiotics (Kvesitadze et al., 2006).

Many researchers have conducted phytoremediation studies using different types of plants to remediate soil contaminated with petroleum hydrocarbon and soil contaminated with heavy metals and other pollutants. Cook and Hesterberg (2013) published a summary of major plants (trees and grasses) currently used in phytoremediation which adsorp or degrade contaminants. Other researchers including Dadrasnia and Agamuthu (2013); Cartmill et al. (2014) and Agamuthu et al. (2010) described phytoremediation of petroleum contaminated soil by several plants with addition of organic fertilizer to enhance remediation.

9.17.1 **Phytoextraction, phytoaccumulation, phytoabsorption, phytosequestration**

This involves the uptake, translocation, accumulation and concentration of contaminants from the environment by the plant roots into the aboveground portion of the plants with subsequent harvesting of the plant tissue (Razzaq, 2017). Phytoextraction is mostly used for treatment of contaminated soils and surface water and groundwater. Phytoextraction involves periodic harvesting of the plant biomass in order to reduce the contaminant concentration in the polluted environment. The use of phytoextraction is mostly limited to metals and inorganic compounds in soil, sediments, surfacewater and groundwater (Rock et al., 2000). It involves a continuous process using metal hyper-accumulating plants or may be induced using chemicals that increase bioavailability of metals in the impacted soil (Greipsson 2011). Continuous phytoextraction depends on the ability of the plants to accumulate contaminants gradually into the plant biomass. Certain plants are capable of hyperaccumulating metals without any adverse effects. After the plant growth in the contaminated soil, they are usually harvested and composted or incinerated to recycle the metals (Ahalya and Ramachandra, 2006).

9.17.2 **Phytostabilisation (phytoimmobilisation)**

This technique immobilizes the contaminants in the soil by using plants with ability to stabilize the contaminants, thus reducing the mobility of the contaminants by preventing leaching, erosion or run off and transform contaminants into less bioavailable forms through rhizospheric precipitation to prevent migration into the groundwater or air (Razzaq, 2017; Lim et al., 2016; Singh 2012; Pillon-Smith, 2005). The process involves humification (the incorporation of contaminants into the soil humus with subsequent lower bioavailability); lignification (the toxic contaminants are irreversibly trapped in the plant cell walls); binding (the contaminants are increasingly unavailable due to irreversible binding into the soil matrix) (Adam, 2001). Plants used in phytostabilisation require extensive root systems for assimilation or absorption and accumulation or concentration within the rhizosphere. Phytostabilisation occurs in the rhizospheric zone, on the root membranes and in the root cells (Byström and Hirtz, 2002). In a study demonstrated by Byström and Hirtz (2002), who investigated phytostabilisation using a shrub plant *Salix viminalis* commonly known as *Osier willow* for phytoremediation of soil contaminated with moderate level of petroleum hydrocarbons. The result obtained showed immobilization of contaminants with increase in concentration within the rhizosphere region from 584 mg/kg to 1018 mg/kg after a period of 10 hours. This implies that phytoimmobilisation occurs within the rhizosphere and reduces the fraction of contaminants in the soil.

9.17.3 **Phytovolatilisation**

This involves the absorption and assimilation of contaminants through the roots of plants with metabolisation and mobilization into volatile form, and transpires with water vapour from the surface of the plant's stems/trunk and leaves (McCutcheon and Schnoor, 2003). In order words, phytovolatilisation involves diffusion of contaminants from the stem of the plant through the leaves to the atmosphere through plant metabolism and plant transpiration. This is suitable for volatile organic compounds such as benzene, toluene, ethylbenzene and xylene (BTEX), naphthalene and trichloroethylene as well as some inorganic compounds that have volatile forms including mercury, arsenic and selenium (Zhu et al., 2010;). This technique does not remove pollutant permanently rather it

transports and transfers pollutants into the atmosphere from one medium to another, thus the pollutant from the atmosphere can be re-deposited into the soil (Razzaq, 2017). The advantage is that contaminants are transformed to less toxic forms while the metabolites released to the atmosphere undergo further degradation process. The limitation or disadvantage includes that contaminant or metabolites may be are released into the atmosphere and may accumulate in vegetation and passed on in plant fruits which may be consumed by humans or animals (Rock et al., 2000).

9.17.4 **Phytodegradation (phytotransformation)**

In phytodegradation, this involves the breakdown of contaminants absorbed by the plant systems through several metabolic processes that occur within the plant tissues, it also involves the breakdown of contaminants external to the plants through the actions of enzymes such as dehalogenase, laccase and nitroreductase, that function as catalysts to the chemical processes that cause transformation and degradation process. Phytodegradation mechanism involves plant uptake and metabolism indicating that for phytodegradation to occur, the contaminants have to be absorbed or assimilated by the plant and translocated within the plant tissues. The uptake of contaminants is dependent on the solubility, polarity and hydrophobicity while the plant uptake of contaminants is depended on the plant type, age of plant and physicochemical characteristics of the soil (Hellström, 2004). Hydrophobic compound are more easily absorbed and translocated while very soluble contaminants with low sorption are not taken up on the roots or translocated to the plant tissues (Schnoor et al., 1995). Lipophilic contaminants are adsorbed to the root surfaces but not translocated within the plant tissue. Non-polar molecules with low molecular weight sorbs to the root surfaces whereas polar molecules are absorbed and translocated (Bell, 1992). The advantages of this process is that contaminant degradation can still occur due to enzymes produced by plants in an environment free of microbes. Plants can grow in sterile soil with high contaminant concentration that are toxic to microbes. Its limitation is that toxic degradation products or toxic intermediates are formed and the identity of the metabolites are difficult to determine (Komossa et al., 1995). In a study demonstrated by Palmroth et al. (2012), who conducted phytoremediation of diesel fuel contaminated subartic soil using several plants comprising herbaceous plants, legumes and grasses. The result obtained showed low concentration of diesel components were found in the roots of the grass while none was detected in the roots of the legumes. It confirmed that plants accelerate the removal of the pollutants in contaminated soil.

9.17.5 **Rhizodegradation**

This involves the breakdown of contaminants in the soil through enhanced microbial processes in the rhizosphere zone. Rhizodegradation is also known as plant assisted *in situ* biodegradation, plant-assisted bioremediation/biodegradation and enhanced rhizosphere bioremediation/biodegradation (Rock et al., 2000). The presence of microbes and their activities in the rhizosphere can increase due to the secretion of exudates, which result in the increase of degradative activity in the soil. The rhizosphere provides the surface area for microbial activity. The microbes benefit the plant by providing the nutrients such as vitamins, cytokins and amino acids for plant growth whereas the plant roots provide suitable habitat where microbial degradation can be stimulated (Qixing et

al., 2011). The root exudates including sugar, amino acids, sterols, nucleotides, growth factors, flavanone, enzymes, organic acids and other compounds synthesized by the plants are released from the roots (Schnoor et al., 1995). Degradation of the plant exudates leads to co-metabolism of contaminants in the root zone. The plant roots increase soil aeration, moisture content and favourable habitat for autochthonous microbes. The stimulation of soil microbes by the plant exudates causes alteration of the soil geochemical characteristics such as the pH which causes changes in the translocation of contaminants (Mahjoub, 2014). The advantages of rhizodegradation include destruction of contaminant occurring *in situ*, translocation of compounds to plants and atmosphere lower than other phytoremediation methods and mineralization of contaminants.

Rhizodegradation disadvantages include the following; (i) - the need for substantial time for development of extensive root system. (ii) - limitation in root depth due to soil physical structure and moisture content of the soil. (iii) - plants require addition of fertilizers due to the microbial competition. (iv) - exudates stimulate other microbes that are not essential for degradation at the expense of degraders. (v) - organic fertilizer from plant may serve as carbon source instead of the contaminant thereby reducing the amount of contaminants being degraded (Rock et al., 2000). Many researchers believe that the main mechanism for phytoremediation is rhizodegradation, but this area has been investigated in phytoremediation (Lim et al., 2016). In a study demonstrated by Muratova et al. (2003), who conducted rhizodegradation using reed plant on bitumen contaminated soil recorded a growth in the number of microbial degraders in the root zone from 2.4 x 10^6 CFU/g to 4.3 x 106 CFU/g. The result obtained showed removal efficiency of 82% after the incubation period. In a similar study demonstrated by Agamuthu et al. (2010), who conducted phytoremediation of engine oil contaminated soil using plants *Jatropha curcas* and *Hibiscus cannabinus* and enhanced with organic wastes indicated an increase in hydrocarbon degrading bacteria in the root zone. The results obtained showed removal efficiency of 96.6% for *Jatropha curcas* and 91.8% for *Hibiscus cannabinus* after 180 days and 90 days respectively.

9.17.6 **Rhizofiltration**

This is the use of roots of plants to absorb, concentrate, precipitate and remove contaminants from wastewater, surface water and groundwater. In this process, contaminants adsorbed onto the surface of the plant roots or absorbed by the plant roots. Initially, plants are allowed to acclimatize with the pollutants before applying for remediation. They are grown hydroponically in nursery until stable large root systems developed. The plants are then transferred to the contaminated water to absorb or adsorb the contaminants. Once the plant roots become saturated, they are harvested and disposed (Sharma 2012). The roots of the plants are efficient in translocating the contaminants such as heavy metals to the shoots. Rhizofiltration is particularly effective in sites with low concentration of contaminants with large volume of water. Several hyperaccumulating plants such as *Pistia stratiotes, Thlaspi caerulescens, Brassica campestris, Sedum alfredi* and *Arabidopsis halleri* have been used in rhizofiltration to remove heavy metals such as lead (Pb), nickel (Ni), zinc (Zn) and cadmium (Cd) from contaminated soil, surface water and groundwater (Abubakar et al., 2014). Lead (Pb) is accumulated in the roots due to the plant physiological barriers for metal transport to the

shoots whereas other metals such as cadmium (Cd) is carried to the shoot of the plants (Kumar et al., 2017).

9.17.7 **Phytohydraulics, hydraulic plume control**

This involves the use of plants with deep root systems (mostly trees) to hydraulically contain, sequester, degrade, remove and mitigate contaminants from groundwater, surface water and soil through uptake and consumption in order to control movement or migration and leaching of contaminants (Arnold et al., 2007; Barac et al., 2009; Rock et al., 2000). Hydraulic control by plants occur within the rhizosphere zone or within the depth influenced by the plant roots. The effective root depth of plant is approximately 1 to 4 feet. Some trees and woody plants are used to remediate and clean groundwater in water table depth of 30 feet (Gatliff, 1994). The plant roots above the water table influence the contaminants in the groundwater through capillary fringe (Sheppard and Evenden, 1985). In hydraulic plume control, deciduous trees such as poplar trees (Populus), willow trees (Salix) and pine trees are utilized because they grow faster, and have deep rooting systems that draw water from the saturated zone (Ferro et al., 2013). These trees have shown remarkable successes in containing plume of organic contaminants such as benzene, toluene, ethylbenzene and xylene (BTEX) and methyl-tert-butyl-ether (MTBE) (Hong et al., 2001). Extraction of groundwater, surface water and soil water by these tree plants depend on the water balance of the site, age of the tree, tree density, depth of groundwater and the potential phytotoxicity of the contaminated plume (Nichols et al., 2014). Most of the studies on phytohydraulics were implemented at sites with shallow contaminated groundwater with depth not more than 3 metres whereas few studies have used trees to reach depth more than 4 metres below ground surface for hydraulic containment of mixture of gasoline and diesel fuels contaminated site (Ferror et al., 2013). In a study demonstrated by Nicols et al. (2009), who conducted phytohydraulic plume control using hybrid poplars, willows and pine trees to contain shallow aquifer contaminated with petroleum hydrocarbons. The result of the soil-gas analyses showed 95% mass loss for total petroleum hydrocarbon (TPH), and 99% for benzene, toluene, ethylbenzene and xylene (BTEX).

9.17.8 **Vegetative cover systems, evaporatranspiration covers system**

This is a long term and a self-sustaining system of using plants to grow in and or over soil contaminated with toxic substance or materials that pose environmental risk (Rock et al., 2000). This system controls moisture and percolation, and promote surface water runoff. It also minimizes erosion, reduces leachate formation and prevents direct exposure to the contaminants and contact with receptors (Mahjoub, 2014). In addition, vegetative cover systems reduce the risk of the contaminant to an acceptable level with least maintenance. A vegetative cover system comprises evapotranspiration cover and phytoremediation cover. In evapotranspiration, the cover is composed of soil and plants engineered to manage the available soil storage capacity, transpiration process to reduce infiltration of water and contaminants, and rate of evaporation but do not contain barrier layers. The cover forms a layer of monolithic soil with adequate soil thickness that retains infiltrated water and contaminants from migration until removed by evaporation and transpiration processes (Rock et al., 2000). Evapotranspiration covers use two natural processes to control infiltration into the contaminants. The soil serves as a water reservoir, whereas

the natural evaporation from the soil together with plant transpiration empties the soil water reservoir before infiltration into the contaminated layer and generate leachate. However, to minimize percolation, conventional cover system consisting of geo-membranes, geosynthetic clay liners and compacted clay with low permeability barrier layers are often utilized but this is expensive (Mahjoub, 2014). In addition to removing large amount of water from soil to the atmosphere, vegetative cover system accumulate, transfer and destroy contaminants found in the vadose zone and shallow groundwater underlying contaminants (Mahjoub, 2014).

9.18 **Bioelectrochemical system, electrobioremediation *(in situ and ex situ)***

This is a trans-disciplinary system that relies on the use of electro-active microbes to catalyze the oxidation or reduction reactions of organic and inorganic electron donors and deliver electrons to the solid-state electrode (anode), with subsequent transfer or exchange of electrons to the solid-state electrode (cathode) through a conducive circuit and simultaneously generating energy. (Srikanth et al., 2018; Srikanth et al., 2016; Wang et al., 2015). This system is mostly deployed in contaminated media as unlimited electron acceptors or donors (Lai et al., 2017; Zhang et al., 2013). In order words, it is a system that converts chemical energy from organic wastes or contaminants to electrical energy and hydrogen or value added chemical products, and working on interface of electrochemistry and fermentation (Srikanth et al., 2016). Bioelectrochemical system can be classified based on the application of microbial fuel cells for power generation, microbial electrolytic cells for biofuel production, microbial desalination cell for saline water desalination, and microbial electrosynthetic cells for synthesizing value added products. In a study demonstrated by Daghio et al. (2017), indicated that biolectrochemical systems can be employed to energize and stimulate anaerobic oxidation of different types of organic waste to reduced contaminants in soil and groundwater, including petroleum hydrocarbons, and chlorinated compounds. The advantages of biolectrochemical system include the possibility to promote complete oxidation without addition of oxygen or electron acceptors, and the possibility of co-localization of microbes and electron acceptors as well as the possibility to monitor and control biodegradation reaction (Daghio et al., 2017). In a laboratory study demonstrated by Palma et al. (2017), who conducted bioelectrochemical treatment of hydrocarbon contaminated groundwater. The results obtained showed that phenols were gradually removed from 12% to 50% while electric current generation gradually increased from 0.3 mA to approximately 1.9 mA. On the average, the phenol removal rate and the coulombic efficiency were 23 ± 1 $mgl^{-1}d$ and 72 ± 8%. The performance of the system was enhanced following bioaugmentation with wastewater which harboured microbes that are capable of anaerobic oxidation using solid-state graphite granules as electron acceptors.

9.19 **Nanobioremediation, nanoremediation *(in situ and ex situ)***

Nanoremediation is the use of reactive nanomaterials (NMs) or nanoparticles (NPs) or nanostructure materials (NSMs) or nanocomposites (NCMPs) or nanoclusters (NCs) that exhibit unique physical, chemical and biochemical properties in enzyme mediated remediation, transformation and detoxification of persistent hydrophobic contaminant and toxicants (Rizwan and Ahmed, 2018; Galdames et al., 2017; Yadav et al., 2017; Karn et al., 2009). These materials or particles are engineered or formed by plants or

microorganism, and comprise particles with at least one dimension measuring between 1.0-100 nm (Kumari and Singh, 2016; Thomé et al., 2015). They are classified into (i) – carbon-based (carbon fullerenes) and carbon nanotubes, (ii) – metal-based (quantum dots, nano zero-valent iron (nZVI), nanosilver, nanogold and nanosized metal oxides (ZnO, Fe_3O_4, TiO_2, CeO_2)., (iii) – Dendrimers or nanopolymers, (iv) – Composite or bulk-type materials (Nnaji, 2017). Nanomaterial or nanoparticles have properties that allow catalysis and chemical reduction to mitigate the contaminants. As reducing agents, the particles degrade organic contaminants and change the oxidation state of elements, and combined with catalytic enhancement of redox reactions implies their functionality in soil and groundwater remediation (Nnaji, 2017).

For *in situ* nanoremediation, no groundwater is pumped out for aboveground treatment, and no soil is excavated or transported to different location for disposal and treatment (Otto et al., 2008). With their minute size and innovative surface coating, these particles pervade tiny spaces in the subsurface and remain dispersed in groundwater, allowing the particles to move and migrate farer than larger or micro or macro sized particles and achieve wider distribution (Karn et al., 2009). The mobility of natural or synthetic nanoparticles depends on dispersion, aggregation, settling and formation of mobile clusters. Nanoparticle such as zeolites, carbon nanotubes and fibres, metal oxides, titanium dioxide, enzymes and noble metals such as bimetallic nanoparticles (BNPs) have been used successfully in remediation of contaminants. Out of these, the most widely used is the nanoscale zero-valent iron (nZVI) which are modified with inclusion of palladium as catalyst for improved performance (NanoRem, 2016). Detailed and comprehensive overviews of chemistry and engineering of nanotechnology applications are described by Zhang (2003) and Theron et al. (2008). In a study demonstrated by Reddy et al. (2011), who conducted nanoremediation using nanoscale iron for degradation of organic compound dinitrotoluene (DNT) in the soil. The results obtained showed 41-65% removal of DNT near the anode while removal was 30-34% near the cathode. The highest removal was recorded using lactate modified nanoscale iron particles. However, the overall degradation of DNT was due to nanoscale iron particles with the electrochemical process enhanced the delivery of nanoscale particles in degradation of organic contaminants.

10. Physicochemical treatment methods

The physicochemical methods encompassed remediation, recovery and containment technologies that uses physical and mechanical barriers to isolate, recover or separate contaminants in the soil, sediments, surface water and groundwater. The physicochemical treatment is mostly done *in situ* or *ex situ* and comprises different techniques such as soil isolation and containment, containment booms and skimmers for surface water, physical barriers, surface capping, hydraulic containment, pump and treat, soil vapour extraction, steam stripping, air sparging, soil flushing, vacuum pumping, steam-induced volatilization.

10.1 Isolation and containment *(in situ)*

This technique uses physical barriers and mechanical barriers to minimize, restrict and prevent the contaminants from further movement such as the horizontal and vertical migration, seepage, permeability and leaching in the soil, sediments and groundwater, and prevent and restrict spreading on surface water to avoid reaching potential receptors

such as biologically sensitive environments (Jankaite and Vasarevicius, 2005). This technique uses vertical and horizontal barriers made of steel, bentonite, cement and retaining walls, asphalt or concrete for soil isolation and containment and hydraulic control for groundwater while booms and skimmers are used for surface water at the sea. For soil isolation and containment, they are mostly deployed when subsurface contamination precludes excavation and removal of soil (Jankaite and Vasarevicius, 2005; Lombi et al., 1998). For surface water, they are deployed as immediate emergency response option for spillage to isolate and contain oil spillage at sea. However, isolation and containment process are effective and acceptable management remedial option but requires adequate expertise and monitoring. However, in theory, there is no limit to the contaminant concentration which can be contained in any given site (Ibrahim, 2009).

10.1.1 **Containment booms *(in situ)***

Containment booms are used as spill response option for recovery and containment of petroleum hydrocarbons, crude oil, hydrophobic organic compounds, non-aqueous phase liquids (NAPLs) spill on the surface of water at the sea in order to prevent oil slicks from moving away to affect the coastal shoreline. They consist of air-filled or foam-filled compartments or floatation chambers to provide buoyancy with skirts that hang below the water surface or the sea surface. The skirts are supported by ballast chains and cables to absorb the tensional forces exerted on the booms and provide weight to maintain vertical orientation of the booms. The main function of the booms is to provide a physical and floating mechanical barrier to encounter and contain oil slicks at sea to limit spreading, evaporation, fragmentation, dissolution, emulsification and natural dispersion, to protect the biologically sensitive areas, and to divert oil to areas where it can be recovered, collected and treated (IPIECA-IOGP, 2015; Michel, 2015). Once deployed at sea, the booms are anchored and towed into the spilled oil using two boats or vessels in a “U”, “J” or “V” configuration to form swathe width (Michel, 2015). The configuration is formed by the current and waves which push against the centre of the boom. Containment booms are categorized into curtain booms and fence booms based on their design. Once the spilled oil are encountered they become concentrated at the apex of the booms where further clean up treatment can be applied. The performance and the ability of the boom to contain oil are influenced by water current, wind and waves (ITOPF, 2011).

10.1.2 **Skimmers *(in situ)***

Skimmers are mechanical barriers designed to remove floating oil (oil slicks) from the water surface at sea before it reaches the sensitive coastline, and are classified based on the area where they are used such as inshore, offshore, in shallow water or in rivers. Skimmers are designed to recover oil in preference to water, and are in form of belt, disc, drum, mop and floating suction with never ending surface for spill oil to cling to (Agrusta et al., 2013). They may be self-propelled-moved, dynamic and stationary based on the way they recover oil. They are classified into four groups based on the principle of operation and mechanism such as weir system which relies on gravity, oleophilic system which relies on adhesion of oil to a moving surface, mechanical system which relies on the physical picking of oil by scoops, belts or grabs, and vacuum system which relies on pumps and suction (ITOPF, 2012). The effectiveness of a skimmer is determined by how well and fast it collects the oil, and how much water it collects in the mix. The oil

collected by the skimmer is stored in a temporary containment tanks. The advantages of skimmers include physically removal of oil slicks from the environment, it allows recycling and proper disposal of the recovered oil, and minimizes the direct environmental impacts in the open water. On the downside, limitations of mechanical recovery exist. Wind, waves and current affect the performance of the spilled oil to be contained and recovered. Good understanding of the hydrodynamic processes is required and be evaluated by an experienced response team personnel. Over dependence on the mechanical strategies affects the skimmers as the booms fails, skimmers may clog (RRT6, 2006).

10.1.3 **Physical barriers (in situ)**

These are subsurface barriers used to minimize or prevent the horizontal movement or lateral migration of contaminants in soil and groundwater. In remediation design, physical barriers are used to limit the flow of contaminants away from the site as well as to restrict the flow of uncontaminated groundwater onto the impacted site. They divert or redirect groundwater flow around the contaminated zone and contain the contaminants within the barrier (Wagner and Yarmak, 2017). Vertical barriers can serve as resistive barriers or reactive barriers (ANZECC, 1999). Sometimes these barriers are used in sensitive environment where human activities are located downstream from the site. The vertical barriers mostly used are slurry trench walls, geomembrane walls, grout curtains, plastic or sheet pilings cutoff walls, vitrified barriers, frozen barrier, steel shoring, cement and bentonite. Circumferential barriers are used to completely enclose the source of contamination, whereas the open barriers are used to divert or redirect groundwater flow. The subsurface conditions determine the selection of a suitable vertical barrier for a contaminated environment. Slurry walls are mostly used for softer soil while grout curtains are suitable in fracture rock (Runer and Ryan, 1995). Slurry wall consists of a trench down gradient or an excavated trenches around the area of contamination and filled with soil, cement or bentonite. Some compounds affect cement-bentonite vertical barriers because its impermeability decreases in high concentration of creosote, water-soluble salts and fire retardant salts while soil-bentonite mix resist chemical attack (Jankaite and Vasarevicius, 2005). A grout curtain is formed by vertically injecting grout directly into soil borings or holes that are drilled in a regular pattern around the contamination or by *in situ* mixing of soil (Ibrahim, 2009; Gerber and Fayer, 1994). Sheet pilling cut-off walls are formed from precast interlocking sheets of steel, precast concrete, wood or aluminum installed or driven into the impacted soil to a depth of about 12 -30 m. The walls are strong and resistant to chemical attacks (Pearlman, 1999). The vitrified barriers are formed using electrodes to melt the vadose zone of the unsaturated soil at a depth of 9 m *in situ* (Gerber and Fayer, 1994). Frozen barriers are formed in a circumferential pattern to completely enclose a contaminated site through a refrigeration system that create and maintain a frozen barrier, they can be installed as open barriers to redirect the groundwater flow (Hass and Schafers, 2005). However, in general, vertical barriers do not eliminate contamination rather they manage the contamination by restriction and prevention of lateral migration of the contaminants. In a study demonstrated by Chapman and Parker (2005), who conducted an investigation on plume persistence due to aquitard back diffusion following dense non-aqueous phase liquid (DNAPL) source and isolation using a steel sheet piling enclosure for a period of 3 years.

The results obtained in response to DNAPL isolation, three aquifer monitoring wells exhibited strong trichloroethylene (TCE) concentrations decline from 5000 and 30,000 µg/L to values levelling between 200 and 2000 µg/L which indicated that vertical back diffusion with horizontal advection and vertical transverse dispersion account for the distribution of TCE in the aquifer.

10.1.4 **Surface capping *(in situ)***

Surface capping of contaminated soil at a polluted site forms a physical barrier between the contaminated media and the surface. It is usually used to isolate the impacted soil from potential receptors and to limit the infiltration of rainfall as well as shield humans and the environment from the contaminant effect. Surface capping involves covering of the contaminated media with a cap sufficiently thick and impermeable to minimize movement and migration of contaminants to the surface, to prevent contamination of surface water and direct contact of human and animals with the contaminated materials. A suitable cap must restrict or prevent surface water infiltration into the contaminated subsurface to reduce the potential for contaminants to leach or migrate from the impacted site (Mulligan et al., 2001). Thus, reducing and limiting infiltration reduce the potential for downward migration of the contaminants to the groundwater. Surface caps limit and restrict the upward movement of vapour by preventing generation of contaminated dust and volatilization of contaminants. It does not prevent and limit the horizontal movement and migration of contaminants because of the groundwater flow. It can be used together with vertical barriers to produce an effective structure around the contaminated site to form land encapsulation (USEPA, 2007). Surface capping traps and directs vapour to basement where the vapour condensed and subsequently collected. It can be formed using variety of materials such as high-density polyethylene (HDPE) liners, synthetic membranes (geomembranes), asphalt, cement and low permeability soil can be such as clay to provide different degree of protection (Ibrahim, 2009; USEPA, 2007). A typical surface capping usually has a combination of materials layered on top of the other with a layer of vegetative cover applied to the surface to reduce soil erosion, runoff and limit precipitation. In a study demonstrated by Cornelissen et al. (2016), who conducted a large scale field trial surface capping of sediments (sediment to water fluxes) contaminated with polychlorinated dibenzodioxin and dibenzofuran (PCDD/F) with active caps enhanced with powdered activated carbon (PAC) for period of 5 years. The results obtained showed the surface capping effectiveness in reducing fluxes and yielded 80% to 90% for the PAC caps whereas the non-active caps showed decreased level of effectiveness of 20% to 60%. The increasing effectiveness of the PAC containing active caps was as a result of the slow sediment-PAC mass transfer of PCDD/F with bioturbation by the benthic organisms while the decrease in the effectiveness of the non-active caps was as a result of deposition of contaminated particles on top of the surface caps.

10.1.5 **Hydraulic control, hydraulic containment *(in situ)***

This is a containment option for groundwater and involves confining further migration of contaminated plumes within a limit to control movement of contaminated groundwater, thus, restricting or limiting the continued extension of the contaminated zone. It reduces the concentrations of the dissolved contaminants in groundwater effectively that the

aquifer meets the cleanup goals. It relies on pumping the contaminated groundwater to aboveground through extraction wells, treating it at the surface in order to remove the contaminants and then reinjecting the water underground or disposing of it off site by transporting it to a treatment facility. After the containment, according to type and extent of contamination, the contaminated water can be treated by different physical, chemical or biological treatment methods (Mackay et al., 2002). Plume containment consist of numerous extraction wells strategically placed within the plume (Ibrahim, 2009). This is the first process in pump and treat technology for remediation of environment (Mackay et al., 2002). The process is accomplished by three configurations, (i) – a pumping well, (ii) – a subsurface drainage system combined with a pump well, (iii) – a well within a physical barrier system. The configuration may involve continuous permeable reactive barriers (PRBs) to enable flow through their cross-section, funnel and gate systems with permeability to the contaminated water, array of wells filled with permeable reactive barriers and injected systems (Simon et al., 2002). Although, hydraulic containment and cleanup represent separate objectives, remediation efforts are undertaken to achieve a combination of both. In a study demonstrated by Lewis et al. (2008), who conducted an investigation on hydraulic containment system for containment of trichloroethylene (TCE) contaminated groundwater at gaseous diffusion plant. The result obtained after 1 year of installation of hydraulic containment system at the site showed a significant decrease in groundwater potentiometric head in the boundary area.

10.1.6 **Pump and treat *(in situ)***

This technique is primarily for groundwater and soil remediation, and mostly for contaminants such as petroleum hydrocarbon compounds, volatile organic compounds (VOCs), semi volatile organic compounds (SVOCs), fuel oil, metals, chemical compounds dissolved in groundwater. The process involves pumping of groundwater to the aboveground treatment system where the contaminants are removed by other remediation treatment methods such as air stripping, ultraviolet, activated carbon and biodegradation (Zhang, 2009). This technique is used in controlling a hydraulic gradient and keeping a contamination release from migration and spreading further (VanWalt, 2013). The technique has application in many remedial systems that depend on the hydrogeological, remediation objectives and contaminant properties such as where a significant volume of non-aqueous phase liquid (NAPL) is trapped at or below the water table. Sorption and solubility are important chemical characteristics that influence the efficiency of the pump and treat technique. For sorption, once the chemical contaminant reached the subsurface, it interacts with the solid matric of the subsurface and some chemical components dissolve in the groundwater while some sorbed to the solid media (Bedient et al., 1994). For solubility, if the contaminants remain non-aqueous phase liquids (NAPLs), they dissolve gradually into the groundwater and the cleanup goal may not be achieved because it is difficult to reach sufficiently low concentrations because of the equilibrium of absorption and desorption processes in the soil (VanWalt, 2013). Many strategies for managing groundwater contamination using pump and treat technique comprise the hydraulic containment and groundwater quality restoration. Several other physicochemical techniques and biological techniques are used in combination with pump and treat to address the groundwater remediation goal. In the reviews by the USEPA (1992), it was found that in the majority of the studied cases, 15 sites out of 24

sites where pump and treat system were used. The groundwater extraction systems (pump and treat) were able to achieve hydraulic containment of the dissolved phase containment plume and the extraction systems were able to remove substantial amount of contamination from the groundwater.

10.2 **Soil vapor extraction *(in situ and ex situ)***

This technique uses vacuum blowers or vacuum pumps and extraction wells or pressure venting wells to induce adequate gas or air flow through the contaminated unsaturated subsurface area to create a pressure gradient, and volatize the adsorbed contaminants, collect and transport the contaminated soil vapour to extraction wells, and finally treat the contaminants aboveground. (Ma et al., 2016; Simpanen 2016; Dadrasnia et al., 2013). The technique relies on the volatility of the contaminants to enable separation by vaporisation from the vadose zone and mostly ideal for high volatile organic compounds (VOCs) and certain semi-volatile organic compounds. It is specifically useful for remediation of soils underlying active industrial sites and facilities (Fox, 1996). In a pilot scale study demonstrated by Zhang et al. (2015), who conducted soil vapour extraction for remediation of semi volatile organic compound contaminated soil. The results obtained showed that soil vapour extraction achieved a remediation effect of 89% removal for semi volatile organic compounds.

10.3 **Air Stripping and Steam stripping or steam distillation *(in situ or ex situ)***

In air stripping, it involves the process by which contaminated liquid containing mostly volatile and semi volatile organic compounds in wastewater is brought in contact with air (gas) so that unwanted volatile compounds present in the contaminated liquid phase can be released and carried off by the gas (Srinivasan et al., 2008). Steam stripping or steam distillation involves separation of one or more volatile components from a liquid steam by a vapour steam introduced through an injection well into the soil to volatilize or vaporize the volatile and semi volatile organic compounds (Toth and Mizsey, 2015; Dadrasnia et al., 2013; Kulkarni and Kaware, 2013). Air stripping and steam stripping are similar, in contaminated water treatment, contaminated water is heated in a packed or tray column, the combined steam and heat effect, or temperature cause the organic compounds to transform from liquid or aqueous phase to gaseous or vapour phase. The contaminated water is fed at the top of the tray column, and steam or hot gas is fed at the bottom. The steam, hot gas or vapour is injected at the bottom of the tower provides heat. The contaminated vapour is extracted and removed through vacuum extraction, and the contaminants are collected through the process of phase separation and condensation. In the process, dilute mixture of organic compounds in water can be concentrated by this method and the end-product are clean water free of organic compounds (Toth and Mizsey, 2015). This process can either take place in batch or continuous process (Driscoll et al., 2008). The problem associated with steam stripping is when the contaminated water contains solid components, or when solid matter precipitates after steam stripping, it causes fouling and breakdown of the heat exchangers. In a feasibility study demonstrated by Veenis and Heking (2014), who conducted a steam-enhanced remediation using steam in an *in situ* remediation at Greenwich Mohawk site. The results obtained showed that steam stripping has the potential to remove 84% to 100% of most volatile compounds while compounds with less volatility due to lower solubility and

higher vapour pressure tend to remain in the soil. The concentration of the effluent of all the compounds were less than 500 μg/L after the treatments.

10.4 **Soil washing or soil flushing *(in situ and ex situ)***

This process removes contaminants such as volatile and semi volatile organic compounds from soil through washing and scrubbing of the soil with a liquid, and then separate the clean soil from the contaminated soil and flush water (USEPA, 1996). Soil washing or soil flushing is based on the physicochemical processes that occur in the soil, between the soil particles and the washing solution in which they are dispersed (Sharma and Reddy, 2004). The contaminants bind to soil particles (silts and clays) which bind to coarse soil, and separate the contaminated soil and flush waster from the coarse soil (gravels, stones and sands). However, water is usually infiltrated, or injected into the area of contamination, to raise the level of the groundwater. The contamination bearing fluid is collected and sent to aboveground through a mechanical pump for discharge and disposal, or may be recirculated. Sometimes, surfactants or chemical additives are used to enhance flushing (Fabbricino et al., 2018; Godheja et al., 2016; Seo et al., 2015). Soil washing or soil flushing is divided into the following steps – (i) pretreatment, (ii) separation, (iii) coarse grained treatment, (iv) fine grained treatment, (v) process water treatment, (vi) residuals management. However, the process of soil flushing or soil washing reduces the volume of contaminated soil and makes soil washing and soil flushing a pretreatment step for a remediation technique (Sharma and Reddy, 2004). The release of adsorbed substances occur in soil washing when washing solution is mixed with the soil. In this stage, the contaminants are released from the soil particle surface, and dissolution and solubilisation occur due to changes in the pH and result from the acid-base reaction (Hubler and Metz, 2013). The flushwater may cause formation of soluble complexes with the contaminants, and the oxidation reduction reactions result in desorption. In a study demonstrated by Kang et al. (2012), who conducted restoration of contaminated soil using a soil washing system. The results obtained showed total petroleum hydrocarbon (TPH) removal of 97%, while benzo(a)pyrene removal was 73%.

10.5 **Soil extraction, solvent extraction *(in situ and ex situ)***

This involves separation and concentration process using a single or mixture of solvents such as hexane or dichloromethane, chemical surfactants (sodium dodecyl sulphite and alkyl polyglucosides) as extractant to extract, remove and separate organic contaminants from soil. This technique is effective in removing hydrophobic organic contaminants (USEPA, 2001). The effectiveness of soil extraction depends on the contact between the impacted soil and the mixture of solvents (Silva et al., 2005). Solvent-oil mixture is separated by filtration and solvent recovery by distillation process (Al-Zubaidi and Al-Tamimi, 2018; Li et al., 2012; Wu et al., 2013). Solvent extraction has been used for remediation of soil contaminated with chlorinated organic compounds such as polychlorinated biphenyls (PCBs), and petroleum hydrocarbons using mixture of solvents such as ethyl acetate-acetone water (Murena and Gioia, 2009). Solvent extraction process follow two steps, (i) – desorption of contaminants from the solid matrix, (ii) – elution of contaminants from the solid matrix into the extracting fluid. In a study demonstrated by Li et al. (2012), who investigated solvent extraction of petroleum hydrocarbon

contaminated soil using mixture of hexane and acetone. The results obtained showed that 97% of the oil contaminants was removed from the soil.

11. Chemical treatment methods

The chemical treatment methods include remediation technologies that uses chemicals to contain, sequester, precipitate, concentrate, separate and remove contaminants from the polluted soil, surface water and groundwater. The chemical treatment methods involve *in situ* chemical remediation of contaminated environment such as stabilization, solidification, immobilization, dispersion, emulsification, oxidation-reduction, dehalogenation, activated carbon, supercritical fluid oxidation.

11.1 Solidification/stabilization *(in situ and ex situ)*

This is also known as waste fixation. It helps in restricting and preventing the migration and movement of contaminants by locking contaminants in the soil into a durable matrix, or conversion of contaminants to chemically stable form through addition of cementitious binding materials into the contaminated medium to produce an immobile mass or a monolithic block or a clay-like material or a granular particulate that is non-leachable. This technique is achieved through pozzolanic technique, thermoplastic technique, cement-based technique, organic polymer technique and encapsulation technique (Banaszkiewicz et al., 2017; Ba-Naimon and Hamid, 2016; Bikoko and Okonta, 2016; Bates and Hills, 2015). Stabilization relies on additives to reduce the risk posed by the contaminants by converting them into less harmful, less toxic, less soluble and immobile forms. Whereas, solidification depends on the addition of reagents to hazardous materials with subsequent encapsulation into monolithic mass of high structural integrity, less compressibility and permeability (Anderson and Mitchell, 2003). In general, the target contaminant are mostly inorganics, leachable metals and some organic compounds. The technique reduces the contaminants solubility or chemical reactivity, and convert them into less noxious, less mobile and less toxic form. Chemical solidification or stabilization relies on restricting the contaminants mobility or migration by physical or chemical process with the contaminants instead of the contaminant matrix (USEPA, 2006). The contaminant mobility can be reduced through series of processes such as precipitation, complexation and adsorption. The commonly used solidifying or stabilizing agents and materials include portland cement, gypsum, silicates, carbon, phosphates, sulphur based binders and organo-clays (USEPA, 1997). In a study demonstrated by Meegoda (1999), who conducted stabilization/solidification of petroleum-contaminated soil using asphalt emulsions. The result obtained showed that asphalt emulsion stabilized and solidify petroleum contaminated soil to a durable matrix that can serve as a construction material.

11.2 Immobilization *(in situ and ex situ)*

This method involves the control of soil sorption by augmenting the sorption process in the soil through the use of chemicals such as diammonium phosphate to reduce the contaminant solubility in contaminated soil, and help reduce metal solubility, phyto-availability and mobility (Vu and Tran, 2018; Derakhshan et al., 2017; Bolan et al., 2014). It is suitable for high molecular organic compounds containing hetero organometallic compounds. Increased sorption and decreased solubility lower the pollutant transport and redistribution from the contaminated environments. Chemical

immobilization also serves as a reactive barrier to prevent seepage of contaminants from the contaminated sites (Basta and McGowen, 2004). This technique is also useful in regulating biological degradation (Riser-Roberts, 1998). Immobilization alters the original soil metals to more geochemical phase through sorption, precipitation and complexation, and the most applied amendment include cement, clay, zeolite, phosphate, clay, organic compost and microbes (Finžgar et al., 2006). In a study demonstrated by Basta and McGowen (2004), who conducted chemical immobilization using diammonium phosphate, mineral rock phosphate, and limestone to decrease the subsurface heavy metal transport in smelter contaminated soil. The results obtained indicated that diammonium phosphate has the most immobilization effect on cadmium (Cd), lead (Pb) and zinc (Zn) with immobilization efficiency reductions of 94.6%, 98.9% and 95.8% respectively.

11.3 **Dispersion *(in situ)***

This is the breakup of oil slicks into numerous droplets by chemical dispersants or energy provided by the waves and wind to overcome surface tension at the oil-water interface with subsequent degradation by naturally occurring microbes (Gutiérrez, 2017; Rahsepar et al., 2016; IPIECA-IOGP, 2015). Chemical dispersion increases the contaminant toxicity, but when the atmospheric and weather conditions induce the dispersion of the oil slicks, then the addition of dispersants does not increase the contaminant toxicity. Chemical dispersants contain surfactants with surface-active agents, which possess both oil-soluble hydrocarbon chain and a water-soluble group. The chemical surfactants are amphiphilic compounds (containing both hydrophobic and hydrophilic portions) with ability to reduce surface and interfacial tensions, whereas the synthetic surfactants are anionic, cationic, nonionic or amphoteric but only the anionic or nonionic surfactants are used as dispersants for petroleum hydrocarbon compounds. Surfactants can be used in mixtures or with additives such as salts or alcohol, polymers or foams to control mobility (Mulligan et al., 2001). Surfactant mixtures include solvents with dispersing capability and psuedosolubility in water (Pekdemir et al., 2005; Fiocco and Lewis, 1999). Surfactants have been used as penetrants, emulsifiers, adhesives, de-emulsifiers, flocculants, foaming and wetting agents (Mulligan and Gibbs, 1993). However, not all chemical surfactants are effective in dispersion of oil slicks, whereas some are efficient but have disadvantages of being toxic as well as non-degradable (Ventikos et al., 2004). The biodegradability of any surfactant is crucial, otherwise, the surfactants become accumulated in the environment and cause additional environmental contamination (Zolfaghari-Baghbaderani et al., 2012). However, biosurfactants such as rhamnolipids produced by *Pseudomonas aeruginosa* UG2 are effective in removing petroleum hydrocarbon mixture from contaminated soil. Although, the degree of removal depends on the type of contaminants and concentration of the surfactant (Mulligan et al., 2001). The efficiency of biosurfactants in remediation of petroleum hydrocarbon pollution has been used in removal of Exxon Valdez oil from gravel (Harvey et al., 1990). In a study demonstrated by Khodadadi et al. (2012), who conducted treatment of crude oil contaminated soil using biosurfactants (Saponin) coupled with alkali (NaOH) and biopolymer (Xanthan gum) for optimal enhancement. The result obtained showed removal efficiency of 75% for total petroleum hydrocarbon (TPH).

11.4 **Emulsification *(in situ)***

This is the use of chemical emulsifiers to form water-oil emulsion often called "chocolate mousse" or "mousse" by the action of waves which cause changes in the properties and characteristics of the spilled oil (Mishra and Kumar, 2015; ITOFP, 2011; Joye and MacDonald, 2010). This phenomenon occurs in oil polluted water environment. Emulsions are thermodynamically unstable heterogeneous biphasic system due to tendency to decrease the interfacial area and their interfacial energy comprising heterogeneous liquid consisting of two immiscible liquids, with one liquid dispersed and distributed in another in form of droplets called internal phase or droplet phase (Chrisman et al., 2012). The two phases are stabilized by emulsifying agents, surfactants and surface-active agents, and the characteristics of the emulsion are constantly changing until completed and influenced by temperature, pressure, agitation and time. Their stability is determined by type and amount of surface-active agents with the surfactants present, because surfactants lower the interfacial tension that causes the reduction in droplet size (Tadros, 2013). Several methods used in emulsification includes simple pipe flow (low agitation energy), static mixers, high-speed mixers, colloid mills, high-pressure homogenizer and ultrasound generators. The preparation methods can be a continuous or a batch-wise, and in either methods, there is liquid flow (Tadros, 2013). In water-oil (w/o) emulsion, the dispersed water droplets are encapsulated by the oil matrix, and without a surface-active agents, the water-oil emulsions are not stable, they split back into their original phase due to the high interfacial tension between the two liquids when given enough time (Umar et al., 2018; Issaka et al., 2015). In a study demonstrated by Ashrafizadeh et al. (2012), who conducted emulsification of petroleum hydrocarbon (heavy crude oil) using natural surfactants. The results obtained revealed that addition of natural surfactant increased the stability of oil-water (w/o) emulsion due to decrease in the oil-water interfacial tensions caused by the surfactants. Thus, lowering of the interfacial tension in oil-water (w/o) emulsion is a requirement for remediation of petroleum hydrocarbon contaminants in water environment.

11.5 **Chemical oxidation-reduction *(in situ)***

This technique is also known as *in situ* chemical oxidation process (ISCO). The process involves the introduction of chemical oxidants such as permanganate (MnO_4^-), hydroxyl radical ($\bullet OH^-$), sulphate radical ($\bullet SO_4^-$), ozone (O_3), ferrous iron (Fe^{2+}), sodium persulfate ($Na_2S_2O_8^{2-}$), hydrogen peroxide (H_2O_2) and oxygen (O_2) into the subsurface soil and groundwater contaminated with organic compounds with subsequent transformation, destruction and conversion of the contaminants into non-hazardous, less toxic compounds. The converted organic compounds form stable, less mobile and inert compounds that may undergo further treatments (Besha et al., 2018; Simpanen, 2016; Achille and Yalian, 2010; Kluck and Achari, 2004). This process may involve injection of the oxidants and catalysts into the subsurface of the contaminated soil. The oxidants then react with the contaminants resulting to destruction and decomposition with production of innocuous compounds such as carbon dioxide (CO_2), water (H_2O) and inorganic chlorides (ITRC, 2000). The persistent of the oxidants in the subsurface affects the contact time for migration (advective and diffusive transport) and delivery of oxidants into the targeted area in the subsurface (Huling and Pivets, 2006). The chemical oxidation is dependent on contact between the contaminants and the oxidants. Deployment of this method requires careful site screening and characterisation to

determine the physicochemical properties of the impacted site such as natural organic matter, contaminant mass, chemical oxygen demand, dissolved oxygen, pH of the soil and the groundwater, hydraulic conductivity, soil characterization, groundwater gradient, vadose zone permeability, oxidation-reduction potential, conductivity and resistivity of groundwater. Whereas on the contrary, failure for subsurface heterogeneities and soil permeability may result in pockets of untreated contaminants at the targeted area and the oxidants may be consumed by the soil organic matter and dissolved metals instead of the contaminants, resulting into ineffective treatment (ITRC, 2000). In a study demonstrated by Chen et al. (2012), who conducted *in situ* chemical oxidation (ISCO) remediation on diesel contaminated soil. The results obtained revealed diesel removal efficiency by permanganate, persulfate, and hydrogen peroxide under different concentrations (1%, 3%, 5% and 10%) ranged from 48% to 93% within reaction period of 120 days. The performance and the removal efficiency for the contaminants in the oxidant systems showed hydrogen peroxide < permanganate < persulfate and the oxidant persistence was positively correlated with the contaminant removal performance.

11.6 **Reductive dehalogenation or dechlorination *(in situ)***

This is a subsurface remediation process involving the addition of reagents to soil, surface water and ground water contaminated with halogenated organic compounds containing chlorine, bromine and iodine. Dehalogenation process is achieved through replacement of the halogen molecules by a hydrogen atom with decomposition and partial volatilization of the contaminants (Yang et al., 2015; Peters et al., 2014; Hara, 2012; Damgaard, 2012). Dehalogenation of aromatic compounds occur under anaerobic condition by two mechanism comprising reduction and hydrolysis. Reductive mechanism (reduction) involves anaerobic removal of halogens from homocyclic aromatic rings whereas hydrolytic mechanism (hydrolysis) involves chemical and enzymatic removal of halogens from heterocyclic aromatic compounds (Sims et al., 1991). Many halogenated aromatic compounds are degraded by reductive dehalogenation process. The reductive dehalogenation occurs rarely in a well-aerated environment and the reaction is designated by their specificity for compounds with a particular chemical attributes. The specificity also depends on the position of the aromatic benzene ring with a class of compound. In hydrolytic dehalogenation, a hydroxyl group replaces a halogen, and anaerobic hydrolytic removal of halogen substituents from homocyclic aromatic compounds is rare (Kuhn and Suflita, 1989). Hydrolytic dehalogenation removes halogens from heterocyclic aromatic compounds under anaerobic conditions (Adrian and Suflita, 1989). Reductive dehalogenation has been reported to occur with some bacterial species including mesophilic and thermophilic methanogens. These microbes have catalyzed reductive dehalogenation of aliphatic compounds. However, some of the reactions are heat-resistant and not enzymatically mediated. For non-aromatic compounds, reductive dehalogenations are catalyzed by transition metal complexes, with or without enzyme mediation (Kuhn and Suflita, 1989). Recent reviews have evaluated reductive dehalogenation of polychlorinated biphenyl (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polybrominated diphenyl ethers (PBDEs) but less are known for dehalogenation processes in fresh water, marine and estuarine environments (Haggblom et al., 2003). In a study demonstrated by Zanaroli et al. (2015), who conducted a review on microbial dehalogenation of organohalides in marine and estuarine environments

reported the reductive debromination of a hexa-brominated diphenyl ethers (hexa-BDE) in marine sediments, mangrove marine sediments and freshwater pond sediments incubated in synthetic media. The results reported extensive reductive debromination efficiency of 98% after 90 days in mangrove sediments followed by marine sediment and the freshwater pond sediments.

11.7 **Ultraviolet oxidation, photocatalytic oxidation *(in situ)***

This is an advanced oxidation process which involves the use of ultraviolet radiation or light (UV) and chemical oxidants such as ozone (O_3) and hydrogen peroxide (H_2O_2) to degrade and mineralize organic contaminants and recalcitrant compounds in groundwater contaminated with volatile organic compounds (VOCs) and petroleum hydrocarbon compounds (Suzuki et al., 2016; Umar and Abdul-Aziz, 2013; TECHNEAU, 2010). In this process, high intensity ultraviolent light combines with hydrogen peroxide (H_2O_2) are used to oxidize contaminants to water (H_2O), carbon dioxide (CO_2) and inorganic salt (Trach, 1996). During photocatalysis, the ultraviolet light reacts with hydrogen peroxide by activation of atomic bonds making the molecules more oxidizable to generate highly reactive hydroxyl radicals (OH•) which react the contaminant molecules with subsequent destruction of the parent contaminant compound. However, depending of the chemical structure of the contaminant molecules, the hydroxyl radical reaction pathway includes addition reaction and subtraction reactions or a combination of both with subsequent mineralization of organic contaminants (Trach, 1996; Glaze, 1993). In a study demonstrated by Pueh (2010), who conducted a photocatalytic remediation of organic contaminants in groundwater. Ultraviolent light was illuminated on titanium dioxide (TiO_2) which serves as catalyst to generate highly reactive oxidizing agents such as superoxide, hydroxyl (OH^-) in the presence of oxygen. The results obtained showed an overall methyl tert butyl ether (MTBE) removal efficiency of 80% in 48 hours.

11.8 **Activated carbon treatment *(in situ)***

This involves the adsorption of organic contaminants on to the surface of an activated carbon filter from surface water, groundwater, wastewater and soil. It is effective in reducing and removing the bioavailability of certain organic compounds due to its strong sorption properties, hydrophobicity, high specific surface, microporous structure and its efficiency depends on the nature of activated carbon filter (Aljuboury et al., 2017; Berg, 2017; Okiel et al., 2011, Bucheli and Gustafsson, 2000). Activated carbon has been used in reducing phototoxicity of many herbicides and other chemical compounds in agricultural soil (Vasilyeva et al., 2006). It has a highly porous nature and high surface adsorptive properties with amorphous structure composed primarily of carbon atoms in aromatic configuration joined by random linkages (Koehlert, 2017). It differs from other forms of carbon such as graphite by having sheets or groups of atoms unevenly stacked or oriented in a random manner. The level of distribution depends on the starting material and thermal history. Treatment with activated carbon is based on adsorption whereby molecules of gas or liquid adhere or adsorb on the external or internal surface of an activated carbon. Adsorption of contaminants occurs in microspore with diameter measuring between 0.35 nm to 2 nm. The mesopores and macrospores serve as transport conduits for intra-particle diffusion (Bansal and Goyal, 2005). Under subsurface temperature, adsorption mechanism occurs via a reversible process governed by the van

Der waal force and contaminant desorption occur at equilibrium conditions (Karanfil and Kilduff, 1999). The contaminants removal is controlled by the dynamic equilibrium between adsorption, degradation and contaminant influx, which occur in a biologically activated carbon reactors and contaminants remain in the treatment zone when combined rates of adsorption and degradation exceed the contaminant influx (USEPA, 2018). In a study demonstrated by Kalmykova et al. (2014), who conducted and investigated sorption and degradation of organic pollutants, alkylphenols, bisphenol A (BPA), phthalates and polycyclic aromatic hydrocarbons (PAHs) from landfill leachate using granulated activated carbon and peat filters. The results obtained showed that alkylphenols and bisphenol A were completely removed by granulated activated carbon filters. The polycyclic aromatic hydrocarbons (PAHs) were sorbed and removed in 50% and 63% of the measured occasions in the granulated activated carbon and peat filters.

11.9 **Supercritical fluid extraction and supercritical fluid oxidation *(in situ)***

The supercritical fluid extraction process involves the use of solvents (supercritical fluids) such as carbon dioxide (CO_2), methane, propane, butane, and water as extractants to separate one component from another (matrix). The extraction is usually from the soil matrix such as contaminated soil, but it can also be from liquid such as contaminated surface water, and groundwater (Sapkale et al., 2010). Supercritical fluid oxidation involves oxidation of organic solutes in an aqueous medium by using oxidants such as oxygen or hydrogen peroxide (H_2O_2) at elevated temperature and pressure above critical point of water (374.3^{o}C and 22.12 Mpa) to convert contaminants into simple byproducts (Meskar et al., 2018; Yu et al., 2017; Carr et al., 2015; Busamra, 2014). In supercritical fluid extraction, the mechanism of decontamination is similar to solvent extraction, however, due to the transport properties of supercritical fluid, supercritical extraction is more efficient, less energy intensive, leaves no residue and requires less extraction time. During supercritical fluid extraction, the extraction fluid is pumped to a heating zone, where it is heated to supercritical conditions and then injected into the matrix to diffuse and dissolve the materials to be extracted, and driven by the concentration gradient, the contaminants to be removed move from the matrix to be adsorbed to the fluid (Bretti, 2002). Under hydrothermal processing condition, the contaminants are converted into carbon dioxide, nitrogen and water (Sankula et al., 2014). The fluid density is nearer to liquid phase density, and the permeability and viscosity of the fluid are similar in the gas phase (Motamedimehr et al., 2018). Supercritical fluids have zero surface tension and enter into solid matrix very easily, and the fluid are highly sensitive to any slightest changes in temperature and pressure, and the process depends on the density of the fluid, which can be manipulated by adjusting and controlling the temperature and pressure of the system. The liquid absorbs the pollutant as well as disposes of the same pollutant (Castelo-Grande and Barbosa, 2003). In a study demonstrated by Morselli et al. (1999), who conducted supercritical fluid extraction of petroleum hydrocarbons in a clay-sand soil spiked with saturated and aromatic fractions from crude oil. The results obtained showed best recovery of petroleum hydrocarbon close to 70-100% at temperature of 80^{o}C and 227 atm. The findings also showed that addition of a modifier such as acetone to the supercritical fluid changed the selectivity for the extraction of the contaminants or components making up the crude oil fractions. Thus, acetone modifies the solvent

properties while affecting the swelling action on the matrix and favours the desorption process of the analyte.

11.10 **Encapsulation *(in situ)***

In this technique, contaminated soil is compacted and bonded together in a coating of inert materials that are chemically stable with good resistance to biodegradation. The impacted soils are isolated by low permeability surface caps, cut off walls, slurry walls, grout curtains, synthetic textile and clay caps which limit infiltration to prevent migration or leaching of contaminants to the groundwater (Asghar et al., 2016; Zamani et al., 2014; Camenzuli and Gore, 2013; Khan et al., 2004; Anderson and Mitchell, 2003; Roberstson et al., 2003). In the design and construction of an encapsulation cell, the primary focus include – (i) to prevent direct contact with the contaminated matrix, (ii) – to minimize infiltration in order to limit or prevent leachate generation and migration, (iii) – to achieve long term performance so that the system maintains its integrity over time without need for extensive maintenance (Demack and Baltintova, 2015). The efficacy of encapsulation is highly dependent on the lithology and depth of the contaminants in the existing site (Khan et al., 2004). In a study demonstrated by Wami et al. (2015), who conducted micro-encapsulation using a reactive silicate and an emulsifier on crude oil contaminated soil and investigated the contaminants level and parameters such as total petroleum hydrocarbons and level of migration, mobility and toxicity. The results obtained showed an excellent performance for all contaminants with reduction efficiency from 85% to 99.97% in contaminant level after micro encapsulation and the process did not affect or interfere with the soil porosity and permeability.

12. **Thermal/heat treatment methods**

These treatment methods involve the use of heating systems to bring about volatilization and desorption of organic compounds through increase in heating temperature above 300^{o}C to cause removal of low and high molecular weight petroleum hydrocarbons and volatile and semi-volatile compounds in the contaminated media or cause destruction of contaminants in the media. The methods include thermal desorption, steam injection and extraction, conducive heating, pyrolysis, smouldering combustion, incineration and vitrification.

12.1 **Thermal desorption *(ex-situ and in situ)***

This is based on a physical separation system involving volatilization and desorption of the contaminants from the contaminated soil through direct or indirect application of heat under vacuum or into a carrier gas to separate target contaminants from the impacted soil (Kastanek et al., 2016; Ivshina et al., 2015; Mirsal, 2015). Thermal desorption is achieved through multiple mechanisms such as oxidation, incineration, thermal cracking or pyrolytic reactions and depended on the temperature and oxygen distribution (Vidonish et al., 2016a). Thermal desorption is suitable for volatile and semi-volatile contaminants such as polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbon (TPH), dichlorodiphenyltrichloroethane (DDT), chlorophenol and polychlorinated biphenyls (PCBs) (Liu et al., 2019; Zhao et al., 2019). High molecular hydrocarbons in the presence of low oxygen are pyrolyzed at thermal desorption temperature between 300^{o}C to 550^{o}C while hydrocarbons in presence of oxygen are incinerated at thermal desorption temperature between 100^{o}C to 300^{o}C. As thermal desorption or pyrolysis of

contaminants occur when the soils are heated in the anoxic (without air) or hypoxic (low oxygen) condition, the soil may reach higher temperatures between 800^{o}C to 900^{o}C, at this temperature range, the hydrocarbons undergo thermal cracking. Fuel and heat recovery are possible if the soil moisture is low with high British thermal unit (BTU), and the treated soil re-moisturized in order to decrease dust formation. Both low temperature and high temperature thermal desorption can yield removal efficiency up to 99% for *in situ* and *ex situ* treatments but the treatment time may vary due to process configuration and contaminant composition (Stegemeier et al., 2001; Vidonish et al., 2016b; Zhao et al., 2019). In a study demonstrated by Liu et al. (2019), who conducted *ex situ* thermal desorption of polychlorinated biphenyls (PCBs) contaminated soil in combination with 1% calcium hydroxide $Ca(OH)_2$ in a rotary kiln at varied temperature between 300^{o}C to 600^{o}C. The results obtained showed an effective removal efficiency of 94.0% for PCBs at 600^{o}C. The result also showed the effect of temperature on the PCBs behaviour in soil, the effect of $Ca(OH)_2$ in PCB removal and the optimum condition for thermal desorption process for PCBs.

12.2 **Smouldering combustion *(in situ)***

This is a flameless combustion of substances, which initiates a self-sustaining wave of exothermic combustion (net energy producing) in the presence of fuel and oxygen. Thus, converting organic compounds and an oxidant (oxygen) to carbon dioxide (CO_2), water (H_2O) and energy. However, following ignition of materials, the smoldering combustion reaction occurs in a self-sustaining manner, with no input of external energy or fuel after ignition. The heat and high temperature generated by the reacting contaminants during combustion utilized to preheat and initiate further combustion of contaminants, and propagating a combustion front through the contaminated zone in the presence of sufficient air supply (Grant et al., 2016). The heat and temperature generated by smouldering combustion vary spatially and temporally with average temperature range between 600^{o}C to 1100^{o}C (Switzer et al., 2014; Pape et al., 2015). For a sufficient smouldering combustion, the impacted soils must be permeable enough to allow enough influx of air to the combustion zone. The process requires a minimal heat loss with a minimum concentration of contaminants for reaction to proceed in a self-sustaining manner that allows smouldering heat waves to move with the direction of the air flow (Scholes et al., 2015; Grant et al., 2016). To initiate the process, air injection and heating are required to start the combustion. After ignition, heat injection may stop, while air injection continues throughout the duration of the remediation process. The process is sustained by heat transfer through the impacted soil or the contaminant matrix, while contaminants removal occurs through several mechanisms such as exothermic reaction, desorption and pyrolysis. Prior to smouldering wave, convection and conduction heat the impacted soil causing desorption or pyrolysis when the temperature exceeds the boiling point. Although, ignition of contaminants to initiate smouldering combustion takes several hours, but once ignited, treatment may take several hours to a couple days and can be controlled by adjusting the air flow (Scholes et al., 2015; Vidonish et al., 2016b). In the studies conducted by Pironi et al. (2011) and Switzer et al. (2009), who conducted self-sustaining smouldering combustion on non-aqueous phase liquids (NAPLs). In their results, the extent of remediation was at least 99.5% for crude oil and 99.9% for coal tar while the smouldering combustion was self-sustaining and the removal was from 31,200

mg/kg to 104,000 mg/kg for crude oil while for coal tar, the removal increased from 28,400 mg/kg to 142,000 mg/kg. The process remained self-sustaining and achieved sufficient remediation across a range of initial water concentration 0-177,000 kg/mg in spite of the decreased temperature, extended ignition time and velocity of the reaction front.

12.3 **Incineration** ***(in situ and ex situ)***

This involves the total destruction of contaminants such as petroleum hydrocarbons, chlorinated hydrocarbons, dioxins, polychlorinated biphenyls (PCBs) and other organic compounds through burning or combustion at high temperature ranging between 870^{o}C to 1200^{o}C. The incineration occurs in the rotary kilns, circulating bed combustors fluidized bed reactors, liquid injection incinerators and infrared combustor heaters (Vidonish et al., 2016b; Ivshina et al., 2015; Anthony and Wang 2006). During incineration, inflowing oxygen level are maintained at approximately 10% for volatile organic compounds burning. The oxygen level together with the soil loading must be considered together with the contaminant lower explosion limit, in order to ensure safe incineration (Nyer, 2000). The exhaust fumes and the gaseous products are filtered in the scrubbers and electrostatic precipitators. The catalytic converters turn the gases such as nitrous oxide (N_2O), carbon monoxide (CO) and sulphur dioxide (SO_2) into less toxic gases such as carbon dioxide (CO_2), water (H_2O) vapour and nitrogen (N_2) in order to reduce air pollution and deposition of hazardous pollutants (Morselli et al., 2008). In addition to the soil and gaseous products (flue gas) are left after the treatment can be converted to less toxic gases but the fly ash are mostly disposed in the landfills (Vidonish et al., 2016b). After treatment, soils are re-moisturised for dust control before used in any application. The advantage of incineration over other treatment options is that it provides a complete destruction of hazardous contaminants. Due to use of high temperature for incineration, it is an expensive thermal remediation technology but still valuable because of the effectiveness and applicability in removing a variety of contaminants during incineration. It destroys most hydrocarbons due to flammability and high temperature. Contaminants removal efficiency for incineration is still greater than 99% but still expensive to run. In a study demonstrated by Bucala et al. (1994), who conducted thermal treatment on fuel oil contaminated soil using rapid heating condition. The result obtained showed that at 1000^{o}C per sec, the removal efficiency reached 100% in about 0.7 second. The products generated during the heating were analysed and the results showed significant chemical transformation which occur during higher temperatures above 500^{o}C.

12.4 **Pyrolysis** ***(in situ and ex situ)***

This involves the thermal heating or thermal cracking of soils contaminated with organic compounds, semi organic compounds and oily sludge in an anoxic condition or inert atmosphere at elevated temperatures ranging between 400^{o}C to 1200^{o}C under pressure (Moldoveanu, 2019; Vidonish et al., 2016a; Venderbosch et al., 2010; Mohan et al., 2006). The process involves an endothermic reaction, and transforms contaminants into byproducts such as chars, bio-oil and non-condensable gas that provides additional heat for the pyrolytic process. When soil contaminated with petroleum hydrocarbons undergoes pyrolysis, hydrocarbons are remove through thermal desorption when heated

to boiling temperature. But, when temperature goes between 300^{o}C to 500^{o}C, chemical bonds are broken and highly reactive free radicals are forms which react in a sequence of aromatic condensation reactions to form carbonaceous material (char) (Baker and Kuhlman, 2002). Through char formation, pyrolytic process destroys and removes high molecular weight hydrocarbons (Vidonish et al., 2016b). Several processes such as cracking of alkyl chains, dehydrogenation of naphthenes, condensation of aromatics, dimerisation and oligomerisation reactions involved in the formation of char are discussed in detail in Vidonish et al. (2016a). Pyrolysis has similarity with *ex situ* incineration and thermal desorption but has exception of maintaining an inert atmosphere or anoxic condition. Exclusion of oxygen in the process are achieved through indirect electric heating instead of direct flame heating by a fuel burner as in thermal desorption. The volatile products from the pyrolysis are incinerated, while the chars that are left on the treated soil provide carbon. Lab-scale investigations have confirmed more than 99% removal for total petroleum hydrocarbons (TPH) while maintaining the nutrients and the soil properties that are lost during incineration (Vidonish et al., 2016a). Thus, high molecular weight petroleum hydrocarbons such as petroleum sludge, tars, polycyclic aromatic hydrocarbons (PAHs), fuel oils and refine oil are effectively destroyed using pyrolysis (Yeung, 2010). In a study demonstrated by Vin et al. (2019), who conducted pyrolysis on chlorobenzene under dilute atmosphere and moderate atmospheric pressure 106.7 kPa and temperature range of 500^{o}C to 900^{o}C using a fused silica jet-stirred reactor at 500^{o}C to 1000^{o}C in an aluminum tubular reactor. The results obtained showed that 48.5% maximum chlorobenzene transformation was observed at temperature approximately 900^{o}C at residence time of 2 seconds in the jet stirred reactor whereas, 95% maximum chlorobenzene transformation was observed at temperature approximately 1000^{o}C in the aluminum tubular reactor. In both reactors, the same reaction products were detected, but with high formation of methane and acetylene and, low formation of chlorinated and bicyclic compounds, and formation of a carbonaceous material (char) was observed in both reactors.

12.5 **Vitrification *(in situ and ex situ)***

This involves the use of high temperature heating ranging between 1600^{o}C to 2000^{o}C for conversion of contaminants such as contaminated soil and variety of organic and semi-organic compounds into vitreous products comprising chemical durable glass-like solid, bulk glass, frit and crystals, (Vidonish et al., 2016; Abousnima et al., 2016; Godheja et al., 2016; Yeung, 2010). The technique immobilizes and destroys most contaminants by pyrolysis, and majority of the contaminants are volatilized, while the remaining contaminants are converted to a chemical stable, inert, glass-like and crystalline products (Khan et al., 2004). The molten contaminated soil when cooled rapidly hardens and becomes ten times stronger than concrete and possesses properties comparable with obsidian or basalt rock. The high temperature destroys the organic components and contaminants, resulting in few by-products. Vitrification of contaminants occurs through three main types of processes: electrical heating process, thermal process and plasma arc process. All these processes requires enormous amount of energy per tonne of soil treated (Yeung, 2010).

In electrical processes, it uses electrical resistance energy (high voltage) from graphite electrodes inserted in the contaminated media (soil surface), and electrical current is

supplied to heat the soil to temperature between 1400ºC to 2000ºC. The depth of treatment is usually about 20 feet, and the process relies on the alkali metal oxide content which increases the electrical conductivity, heating and melting temperature. When the silica content of the soil is sufficient enough, the contaminated soil is converted into glass during high temperature heating with the organic matter and contaminants while the inorganic contaminants are converted or encased in the glass like solid monolith that results after treatment. A vapour hood traps the off gases and channels them to a treatment train comprising a quencher to cool the gases, a scrubber, activated carbon and oxidizer.

The thermal processes use external heating system in a refractory-line reactor. The mechanism is similar to the electrical process with exception that external heating systems are used instead of electric voltage whereas in plasma arc processes high temperature heating above 5000ºC through electrical discharge are employed to the contaminated soil (Khan et al., 2004). These processes destroy, remove and immobilize a variety of volatile and semi-volatile organic compounds including polychlorinated biphenyls, dioxins, priority metallic pollutants and radioactive materials or radionuclides (USEPA, 2000). Although contaminated soil can be treated by vitrification, the process is mostly directed towards inorganics and with the complexity, it required a proper and specialized training and skills. As a result, this is employed to treat relatively small amount of contaminants that are difficult to remedy by other remediation methods (Yeung, 2010). In a study demonstrated by Ballesteros et al. (2016), who conducted vitrification of soil contaminated with hexavalent chromium to immobilize the highly toxic industrial waste. The results obtained after treatment formed a vitrified, glassy products with silicate composition with environmental stability, high mechanical resistant properties and chemical stability. These properties were confirmed through toxic characteristics leaching test to determine the lixiviation of the toxic constituents in the vitrified samples. The test result recorded a value of <0.5 mg/l that is in compliance and in respect to the environmental regulatory standards.

13 Electric and electromagnetic treatment methods

This method involves the use of electrical potential energy or electromagnetic energy comprising radio waves, microwaves and light energy to destroy and remove contaminants in the soil through energy transfer to volatilize and desorb low molecular weight hydrocarbons. The method includes electrical resistance heating, radio frequency heating, microwave heating, electrokinetic process and photocatalytic degradation.

13.1 Electrical resistance heating *(in situ)*

Electrical resistance heating is a form of thermal treatment that involves the passing of electrical current through the electrodes to heat contaminated soil and groundwater in order to volatilize the contaminants (Beyke and Fleming, 2005). Electrical current passes through the moisture in soil pores which act as electrical resistor and the resistance to electrical current flow in the soil generates heat greater than 100ºC or boiling point of water, producing vapours, steam and volatile contaminants that are recovered through vacuum extraction wells and delivered to the surface for recovery and further treatment (USEPA, 2012). The electrical energy vaporizes the target contaminants and provides a carrier gas as steam to sweep the volatile compounds to the vapour recovery wells (Beyke

and Fleming, 2005). The steam is condensed and cooled to ambient condition, while the volatile organic compound vapours are treated further with granular activated carbon and oxidation. The soil heating strongly effects the kinetic of the contaminants, due to changes in the vapour pressure, and Henry's Law, contaminants are removed more easily, rapidly and effectively. When electrodes are inserted into the impacted soil through drilling technique, pile-driving and direct push method, they do not only pass the electrical current but also serve as vapour and steam recovery point (Beyke and Fleming, 2005). The vapour treatment includes piping, blowers, tank, condenser, granulated charcoal or thermal oxidation unit. When groundwater or a non-aqueous phase liquid (NAPL) is extracted, a separator tank with water treatment system is installed. The spacing between each electrodes is usually 15 to 20 feet apart and the operation time is mostly less than one year. In the design and cost of this technique, the volume of the impacted media (soil or groundwater) to be treated and the contaminant type are taken in consideration for effective operation. In a case study demonstrated by Beyke and Fleming (2005), who conducted pilot test to determine the feasibility of electrical resistance heating in reducing the trichloroethylene (TCE) concentration and removal of non-aqueous phase liquid (NAPL). In the operation, seven electrodes were used and the heating was extended to the depth of 100 feet and heated to the boiling point of trichloroethylene (TCE) in water while the captured vapours were further treated with granular activated charcoal. The steam was condensed and the condensate was further treated before recycling. The confirmatory results obtained after treatment showed that concentrations of trichloroethylene (TCE) in the treated soil were reduced by 98% whereas the concentrations in the groundwater were reduced by 99%. At the conclusion, the samples from the treatment monitoring wells contained TCE at the concentration below 11 mg/L, which was the contaminant concentration reduction goal of the project.

13.2 **Radio frequency heating *(in situ)***

Radio frequency heating (RFH) involves the use of high frequency (13.56 MHz) of alternating electric field with wavelength of 22 m for heating of soil for volatilization and desorption of low molecular weight organic compounds and hydrocarbons by decreasing viscosity and increasing bioavailability (Vidonish et al., 2016; Godheja et al., 2016; Bientinesi et al., 2015; USEPA, 2006). Radio frequency heating heats the matrix quickly and efficiently by heat transfer on a molecular level, and by imposing electrical field in electric dipoles in the impacted soil and groundwater. It also relies on the molecular dielectric interactions, while heating is marked by direct heat formation in the soil without any heat transfer medium such as hot air, steam and overheated surfaces (Huon et al., 2012). Radio frequency heating removes contaminants by increasing mobility, water solubility, and vapour pressure, while decreasing surface tension and making the adsorption equilibrium in the soil matrix to shift towards desorption (Vidonish et al., 2016). These effects positively have influence on the bioavailability of the contaminants for bioremediation because radio frequency heating single handedly does not remove contaminants but enhances the contaminants removal by increasing the performance of other remediation techniques such as bioremediation, soil vapour extraction and air sparging (Price et al., 1999). The heating causes some physicochemical and biological changes in the properties and characteristics of the impacted soils and groundwater, and

make them amenable to remediation. In radio frequency heating, energy is delivered to the matrix by electromagnetic radiation and not by heat transfer, conduction and fluid convection properties such as soil permeability (Price et al., 1999). A radio frequency heating system unit consists of a remotely operated computer RFH module, a radio frequency generator that provides the electromagnetic energy through the antenna radiators and a matching network which in combination with the antenna applicator insure maximum heat transfer to the impacted soil. The electrical properties of soil (conductivity and dielectric constant) depend on the ability to absorb radio frequency and heat, while the dielectric constant determines the wavelength of the radio frequency energy and conductivity is proportional to the ability to absorb radio frequency energy (Price et al., 1999). In a case study demonstrated by Huon et al. (2012), who conducted *in situ* radio frequency remediation at a former service station using three electrode arrays with extraction wells for soil vapour extraction. Petroleum hydrocarbon contaminants comprising benzene, toluene, ethylbenzene, xylene (BTEX) and mineral oil were removed from the impacted. The results obtained after radio frequency heating treatment in combination with soil vapour extraction yielded 80% reduction in the remediation volume and time when compared to other conventional soil vapour extraction.

13.3 **Microwave heating *(in situ and ex situ)***

This involves the use of electromagnetic radiation with frequencies between infrared and radio frequencies in the frequency range between 300 MHz to 3000 GHz and wavelengths between 1 mm to 1 m to cause volumetric heating in the soil and groundwater. Microwaves having low energy (0.03 kcal/mol) in their photons produce agitation of polar molecules or ions that oscillate under the effect of electromagnetic fields, and cause the molecule dipoles to position in the radiation (polarized). The displacement inside the material and the conduction mechanism generate heat through resistance to electric current that are used for volumetric heating of the contaminants in soil and groundwater. Microwaves with frequency of 2.45 GHz are used in heating of dielectric materials. They are applied in many industrial, scientific and medical applications and are regulated and governed by Federal Communications Commission (FCC) in order to avoid interference with frequencies used for military and communication purposes (Falciglia et al., 2018; Falciglia et al., 2016; Porch et al., 2012; Mutyala et al., 2010; Bradshaw et al., 1998). The materials that interact with microwaves to generate heat are microwave absorbers and the interactions mechanisms between electromagnetic radiations and dielectric materials are described as conductive losses, magnetic losses and dielectric losses and these mechanisms initiates the dielectric heating (microwave heating) that depends on the electromagnetic field characteristics and the material properties (Aguilar-Reynosa et al., 2017; Menéndez et al., 2010). Heat proportion during microwave heating is carried out by ionic conduction and bipolar rotation. In ionic conduction, the free ions, or ionic species and molecules positioned by ionic motion generated by the electric field, result in rapid volumetric heating which is generated by conversion of kinetic energy (Falciglia et al., 2018; Robinson et al., 2009). In biopolar rotation, the molecules position fast as electric field and the movement generates friction with molecule rotation between the molecules, which transfers energy that results into heat because of the molecule rotation. Microwave heating processing is carried out inside of the material, which results to better and sufficient heat transfer with

high energy yield (Krouzek et al., 2018; Aguilar-Reynosa et al., 2017; Falciglia et al., 2013). Microwaves do not destroy the molecular structure of material because of the energy in the chemical bonds and they are considered as non-ionizing radiations. The arousal or excited effect of the molecules generates the kinetic energy that causes heating (Cuevas and Hernández, 2011). In the studies demonstrated by Li et al. (2009) and Sivagami et al. (2019), who conducted microwave heating using carbon fibre and spent graphite respectively in treatment of soil contaminated with petroleum hydrocarbon. In both studies, the impacted soils were heated with microwaves with frequency of 2.45 GHz and carbon fibre and spent graphite were added respectively to improve conversion of microwave energy to thermal energy required to heat the impacted soils, and oil contaminant fumes were removed from the soil matrix through condensation system. The results obtained showed that carbon fibre and spent graphite can effectively enhanced microwave heating of petroleum hydrocarbon contaminated soil. The microwave power, carbon fibre dosage or graphite dosage and microwave irradiating time are vital parameters in removal of contaminants in both studies, and under optimum condition, removal of 99% was achieved using carbon fibre while TPH removal efficiency of 91.18% was achieved using spent graphite.

13.4 **Electrokinetic remediation, electrochemical soil process*(in situ)***

Electrokinetic (EK) remediation involves the use of a low intensity direct current through contaminated media with low hydraulic permeability by appropriately distributed electrode pairs to separate and extract organic compounds, radionuclides and heavy metals from soil, sludge, slurries, sediment and groundwater (Cameselle and Gouveia, 2018). It relies on application of electrical potential gradient between electrodes to stimulate the flow of water and contaminants from anode to cathode as well as migration of contaminants towards the oppositely charged electrodes through various physical and chemical mechanisms such as electrolysis, electrophoresis, electro-migration and electro-osmosis (Istrate et al., 2018; O'Brien et al., 2017; Godheja et al., 2016; Hassan, 2016). When electrical current or voltage passes across electrode pairs that are implanted in a saturated soil matrix, the charged ions, soil particles and water drift towards a particular direction. This movement is referred to as electrokinetics which simply means the physical and chemical transportation of charges, reaction of charged particles and effects of applied electric potentials on formation and fluid transport in porous media (Mosavat et al., 2012; Alshawabkeh, 2001; Cameselle and Gouveia, 2018; Virkutyte et al., 2002).

In electro-migration or ionic migration, it involves the transport of ions or electrically charged particles towards the electrodes. The positively charged chemical species such as heavy metals, ammonium ions and organic compounds in the impacted soil move towards the cathode while the negatively charged chemicals such as chloride, nitrate, phosphate, cyanide, fluoride, and negatively charged organic species move towards the anode when an electric current passes across the soil matrix (Xu et al., 2016; USEPA, 2006). At the anode, hydrogen ions produced during hydrolysis move towards the cathode by the electric field and exchange cationic metals onto surface while the desorbed metal ions are transported towards the cathode. In electro-osmosis, it involves movement of soil moisture generated as a result of movement of ions. When an electric current passes across the moist soil, the soil-water electrolyte acts as an electrochemical

Journal Pre-proof

cell and current passes through the positive anode to the negative cathode. Under the electric potential, a net movement of cations (electroosmotic flow) move towards the cathode as soil pore fluid drags them towards the cathode (Iyer, 2001). Some enhancing solutions, stabilizing agents, surfactants, complex agents, and reagents may be fed at the electrodes to increase the rate of contaminants removal through altering the soil properties such as texture, plasticity, compressibility and permeability (Mosavat et al., 2012). For electrophoresis, when an electric potential is applied on the charged soil clay particles or colloidal suspension, the charged particles together with the contaminants are electrostatically attracted to the electrode and repelled from the other electrode. Thus, the negatively charged clay particles move towards the positive anode (Kim et al., 2015; Mitchell and Soga, 2005). The movement of charged solid particles or colloids is referred to as electrophoresis or cataphoresis (Reddy et al., 2009). Electrolysis of water is the most dominant and most important transfer reaction that occurs at the electrodes in electrokinetic process. In the reaction, the conversion of electrical energy into chemical potential energy creates hydrogen gas (H_2) and hydroxide ion (OH^-) at the cathodes and produces oxygen gas (O_2) and hydrogen ion (H^+) at the anode producing acid at the anode and producing base at the cathode which drift across each electrode (USEPA, 2006). The acid helps to increase the movement of the cationic species in the soil (Saichek and Reddy, 2005). In a study demonstrated by Boulakradeche et al. (2015), who conducted an electrokinetic remediation of hydrophobic organic contaminated soils enhanced using a combination of non-ionic and ionic surfactants. In their study, sodium dodecyl sulfate and Tween 80 with Triton X100 were used as non-ionic and ionic surfactants respectively to enhance the electroremediation. The results obtained after simultaneous use of sodium dodecyl sulphate in the catholyte and Tween 80 in the anolyte increased the removal of n-hexadecane by 69% while anthracene removal was 59% through electro-osmosis. The overall results proved that electrokinetic process are enhanced through application of surfactants.

13.5 **Photocatalytic degradation *(in situ)***

This is the acceleration of chemical transformations using ultraviolet (UV) radiation and photo-catalyst such as titanium oxide (TiO_2), tin oxide (SnO_2), zinc oxide (ZnO), cerium oxide (CeO_2), and other nano-composite semi conductive materials, to promote oxidation reaction and destruction of contaminants in the soil, surface water and sediments (Yang et al., 2017; Khayyat and Roselin 2017; Soroush et al., 2017). The photocatalyst accelerates or speeds up the photoreaction (light induced reaction) by interaction with the substrate in its excited state depending on the mechanism of the photoreaction and the catalyst remain unaltered at the end of the catalytic cycle (Haque et al., 2012). Photocatalysts are invariably semi-conductors, whose reactions are grouped into homogeneous and heterogeneous processes (Saravanan et al., 2017). In homogenous photocatalytic process, metal complexes such as transition metal complexes of iron, nickel, chromium, copper, vanadium etc., are used as catalysts, and under UV radiation and thermal condition, the excited state or higher oxidation state of the metallic ion complexes forms hydroxyl radicals, which react with organic matter that subsequently

result to destruction of contaminants (Saravanan et al., 2017). For heterogeneous photocatalysis, semi conducting materials are used as photocatalysts because of the electronic structure characterized by vacant conduction band and filled valence band, light absorption properties, oxidation or excited states and charge transport properties (Saravanan et al., 2017; Khan et al., 2015). The heterogeneous photocatalysis allows efficient degradation and mineralization of variety of organic contaminants present in low concentrations in the impacted media (Rajamanickam and Shanthi, 2016; Loitta et al., 2009; Mai et al., 2008). The activity of the catalysts in photocatalytic degradation virtually depend on the illumination sources (Igbal et al., 2019). The photocatalytic process is also known as advanced oxidation process, which is suitable for the oxidation of a variety of organic compounds (Umar and Abdul Aziz, 2013). For suitable semiconducting material to act as photocatalyst, the material must be photoactive, capable of a physiochemical change in response to visible light and UV light, biologically and chemically non-reactive, photostable, non-toxic and inexpensive (Saravanan et al., 2017). In a study demonstrated by Pirila et al. (2015), who conducted photocatalytic treatment on organic pollutants diuron (a herbicide), p-coumaric acid (an agro-industrial wastewater), bisphenol A and phthalic anhydride (a plasticizers) in the presence of UV-A irradiation with TiO_2 as photocatalyst. The effects of the photocatalyst loading, pH and concentration were investigated. The results obtained showed that diuron was removed most efficiently with least consumption of energy while bisphenol A was least removed and most difficult to undergo photocatalytic degradation.

14 Acoustic and ultrasonic treatment methods

These treatment methods involve the use of mechanical waves and vibrations to create dynamic oscillations and mechanical effects (compressions and refractions) to generate heat and pressure that induce physical and chemical reactions such as oxidation, adsorption, coagulation, filtration, disinfection, decontamination and stabilization for remediation of contaminants in the soil, sludge, effluents, sediments, slurries, surface water and groundwater. The application of acoustic and ultrasonic treatments include water treatment, soil remediation, waste treatment and recycling, air pollution control and environmental analysis. The process methods include ultrasonic extraction, sonochemical process and acoustic cavitation.

14.1 Ultrasonic extraction *(in situ)*

Ultrasonic extraction involves the application of ultrasonic waves (ultrasound) of frequencies (20 kHz to 2 MHz) for generation of alternating adiabatic compressions and rarefactions cycles on the molecules of liquid medium, with resultant high temperature and pressure to separate solid/liquid in high concentration suspension and decrease stability of water-oil emulsion (Hu et al., 2016; Wu et al., 2013). When ultrasound waves is applied on a medium such as liquid, it generates cyclic succession of expansion (rarefaction and compression phases) which is impacted by mechanical vibrations (Tang, 2003). The compression cycles exerts pressure to force the liquid molecules together, while rarefaction exerts pressure that pulls the molecules apart (Vajnhandl and Marechal, 2005). Ultrasound vibrations lower the thickness of liquid films, increase the gas transfer, decrease coalescence of bubbles and enhance the interfacial area for gas transfer (Adewuyi, 2001). Due to the power of ultrasound in enhancement of physical and chemical reactions and mass transfer, ultrasound extraction are applied in combination

with other treatment processes for environmental protection and remediation of soil, surface water and groundwater (Pham et al., 2009). It provides enhanced mechanical effects for desorption, surface cleaning and leaching (Mason and Collings, 2004). When ultrasonic waves penetrates into the soil matrix which is saturated with contaminants, the contaminants adsorbed at the surface of the solid particles pull apart by shear force and the bonds between the contaminants and soil particles are broken when the solvent transfers high ultrasonic energy into the solid particles and the contaminants. After dislodgement from the soil particles, the contaminants can be separated or be removed by other treatment methods (Song, 2007). Ultrasonicatio helps the desorption of the contaminants in the impacted soil, and also enhances strong oxidant formations (Shrestha et al., 2011; Flores et al 2007). In a study demonstrated by Wulandari and Effendi (2015), who conducted ultrasonic remediation of petroleum contaminated soil in a stainless steel tube reactor using ultrasound frequencies 28 kHz and 48 kHz and input ultrasound power of 220 volts. The results obtained after treatment revealed that the optimum frequency was at 48 kHz with percentage removal of total petroleum hydrocarbon (TPH) at 67.1% while the removal efficiency in solid/liquid ratio 1:3 and 1:10 was 55.6% and 71.4%. The treated soil revealed degradation of long chain hydrocarbon into simpler hydrocarbon compounds.

14.2 **Sonochemical degradation, sonochemical oxidation *(in situ)***

Sound waves comprise alternating compressions and decompressions in a gaseous, solid and liquid medium possessing elastic properties. Sound waves travels longitudinally through a vacuum, gaseous and liquid medium but transversely through solids only (Lapacchini et al., 2017). Sonochemical process involves the exposure of homogeneous and heterogeneous aqueous solutions to high intensity ultrasound waves to produce chemical and mechanical effect through acoustic bubbles referred to as acoustic cavitation (Mullakaev et al., 2018; Rodriquez-Freire, 2016; Li et al., 2013, Lin et al., 2008). The physicochemical effects of ultrasound originate from the direct interaction of molecules with waves and from the acoustic cavitation, nucleation growth and implosive collapse of microbubbles in the aqueous solution. The violent implosive collapse of microbubbles forms the chemically reactive species and emits short bursts of light in sonoluminescence (Pflieger et al., 2014). The bubbles absorb energy from the waves and grow in size with the acoustic cycle until reached an unstable size, and collide or violently collapse. For acoustic cavitation near an extended surface or near big aggregates, asymmetric collapse or implosion causes micro-jet formation of solvent, which collides with the solid surface at tremendous force, resulting in formation of new reactive surfaces with corrosion and erosion. This increases the rate of mass heat transfer near the catalyst surface and the rate of reaction (Pflieger et al., 2014; Song and Li, 2009). Nevertheless, cavitation uses mechanical activation to destroy the attractive forces binding molecules in the liquid phase, application of ultrasonic waves forms compression of the liquid with rarefaction, and high temperatures and pressure initiated by cavitation in the collapsing gas bubbles lead to the thermal desorption causing dissociation of water molecules (•H) and (•OH) (Eren, 2012; Abbasi and Asl, 2008). Ultrasonic irradiation of homogeneous liquids involves gaseous interiors of collapsing cavities, interfacial liquid region between cavitation bubbles and the bulk solution where (•OH) diffuse from the interface (Ozen et al., 2005). The intensity of reaction of ultrasonic irradiation depends on

the frequency of radiation and the applied power and depending on the ultrasonic radiation, only but a small amount of the (•OH) escapes the interfacial region and diffuses back to the bulk solution (Gultekin et al., 2009). However, sonochemical degradation occurs at the gas-liquid interface because of the oxidation of organic molecules by (•OH) in the bulk solution, and thermal decomposition inside the bubbles (Li et al., 2008). Hydrophilic and non-volatile organic compounds are degraded by (•OH) mediated reactions at the interfacial liquid region, while the hydrophobic and volatile organic compounds are degraded thermally inside the bubbles (Eren, 2012; Vajnhandl and Le Marechal, 2007). In a study demonstrated by Kim and Wang (2003), who conducted an ultrasonical enhanced in situ remediation of soil contaminated by non-aqueous phase liquid (NAPL) in soil flushing. The soil flushing was conducted in two conditions, one with 20 kHz frequency and the other without ultrasound irradiation. The results obtained showed that ultrasonication enhanced the removal of oil sufficiently. The degree of the increased removal of oil depended on the frequency, ultrasonic power, washing flow rate and soil type, while increasing the ultrasonic power increased the contaminant removal up to the point where cavitation occurred.

15 Factors affecting selection of a remediation technology

The selection of remediation option primarily depends on a variety of scientific and non-scientific factors, which technically affect remediation efficiency and suitability. Figure 4 illustrates the various biotic and abiotic factors which affect and influence remediation processes and lack of information regarding these factors can influence the process and often reduce the efficacy of the process when implemented. Therefore, in-depth knowledge of the biological properties, environmental properties and the contaminant properties, physicochemical properties, type, composition, concentration, heterogeneity, source, age, material handling characteristics, variable site conditions, geohydrologic conditions, space requirement, process location (in-situ, ex-situ, on-site, in-vessel, off-site,) monitoring difficulties, required level of cleanup standard, extended treatment time, risk management strategy (source reduction, pathway interruption and protection of receptors), remedial approach and strategy, technological suitability and feasibility, outcome (recycling, invasiveness, removal), life-cycle cost-benefit ratio, acceptable risks in residual contaminants remaining after treatment, favourable regulatory perception, ability to achieve the limitations and the ability to conform to space limitation are required for the improvement in remediation and to predict a successful remediation outcome (Kuppusamy et al., 2016a; Kuppusamy et al., 2016b). Some of the non-technical strategy include ability to meet the required clean up standard, acceptable cost relative to other available remediation methods, research and technical factors, human resource factor, economic and liability factor and regulatory factors such as creating markets, controlling the products, toxic substances control act inventory (Boopathy, 2000).

16. Conclusions

This paper provided an overview towards remediation of soil and water environments contaminated with petroleum hydrocarbon and organic compounds. A variety of remediation treatment methods are available but no single method is the most appropriate for all contaminant types and the variety of site-specific conditions that occur at the affected environment. A good understanding of the conditions of the affected environments, nature, composition and properties of the contaminants, fate, transport and distribution of the contaminants, mechanism of

degradation, the interactions and relationships with microorganisms, intrinsic and extrinsic factors affecting remediation and the potential impact of the possible remedial measure determine the choice of a remediation treatment method. More than one remediation treatment method may be required or combined into a process train to effectively remove, contain or destroy contaminants and hazardous materials at the impacted environments.

However, selection of one or more remediation treatment methods is crucial in decision making, as many parameters that conflict in nature play a significant role in decision making. Consequently, it is a good option to select remediation treatment methods that are more adaptive, scientifically defensible, sustainable, non-invasive, eco-friendly and cost effective because cleaning up of pollution caused by petroleum hydrocarbons involves huge, laborious and expensive task.

Acknowledgments

The authors are grateful to the sponsorship from University of Malaya and Centre of Research Grant Management (PG070-2014B) for providing funding for the research.

Journal Pre-proof

References

1. Abatenh, E., Gizaw, B., Tsegaye, Z., Wassie, M., 2017. Application of microorganisms in bioremediation - review. Journal of Environmental Microbiology 1(1), 2-9.
2. Abbasi, M., Asl, N.R., 2008. Sonochemical degradation of Basic Blue 41 dye assisted by nano TiO_2 and H_2O_2. Journal of Hazardous Materials 153 (3), 942-947.
3. Abdel-Shafy, H.I., Mansour, M.S., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Petrol. 25, 107–123.
4. Abdulsalam, S., Bugaje, I., Adefila, S., Ibrahim, S., 2011. Comparison of biostimulation and bioaugmentation for remediation of soil contaminated with spent motor oil. Int. J. Environ. Sci. Technol. 8, 187-194.
5. Abousnina, R.M., Manalo, A., Shiau, J., Lokuge, W., 2016. An overview of oil contaminated sand and its engineering applications. Int. J. of GEOMATE 10(1), 1615-1622.
6. Abubakar, M.M., Ahmad, M.M., Getso, B.U., 2014. Rhizofiltration of heavy metals from eutrophic water using Pistia stratiotes in a controlled environment. IOSR Journal of Environmental Science, Toxicology and Food Technology 8(6), 27-34.
7. Achille, G.N., Yilian, L., 2010, Mineralization of organic compounds in wastewater contaminated with petroleum hydrocarbon using Fenton's Reagent: a kinetic study, J. of American Science, 6(4), 58-66.
8. Adam, G., 2001. A study into the potential of phytoremediation for diesel fuel contaminated soil. Doctoral Thesis. Environmental, Agricultural and Analytical Chemistry, University of Glasgow.
9. Adam, G., Duncan, H.J., 2002. Influence of diesel fuel on seed germination. Environmental. Pollution 120, 363-370.
10. Adams, G.O., Fufeyin, P.T., Okoro, S.E., Ehinomen, I., 2015. Bioremediation, Biostimulation and Bioaugmention: A Review. International Journal of Environmental Bioremediation & Biodegradation 3(1), 28-39.
11. Adewuyi, Y.G., 2001. Sonochemistry: environmental science and engineering applications. Ind. Eng. Chem. Res. 40, 4681-4715.
12. Adrian, N. R., Suflita, J.M., 1989. Reductive dehalogenation of a nitrogen heterocyclic herbicide in anoxic aquifer slurries. Appl. Environ. Microbiol. 56, 292-294.
13. Aeppli, C., Nelson, R.K., Radović, J.R., Carmichael, C.A., Valentine, D.L., and Reddy, C.M., 2014. Recalcitrance and Degradation of Petroleum Biomarkers upon Abiotic and Biotic Natural Weathering of Deepwater Horizon Oil. Environmental Science & Technology 48 (12), 6726-6734.
14. Agamuthu, P., Abioye, P.O., AbdulAziz, A.R., 2010. Phytoremediation of soil contaminated with used lubricant oil using Jatropha curcas. Journal of Hazardous Materials 179(1-3), 891-894.
15. Agarry, S., Latinwo, G.K., 2015. Biodegradation of diesel oil in soil and its enhancement by application of bioventing and amendment with brewery waste effluents as biostimulating-bioaugmentation agents. Journal of Ecological Engineering 16(2), 82-91.
16. Aguilar-Reynosa, A., Romani, A., Rodriguez-Jasso, R., Aguilar, C.N., Garrote, G., Ruiz, H.A., 2017. Microwave heating processing as alternative of pretreatment in second-generation biorefinery: An overview. Energy Conversion and Management136, 50-65.

17. Ahalya, N., Ramachandra, T.V., 2006. Phytoremediation: processes and mechanisms. J Ecobiol. 18(1), 33-38.
18. Al-Daher, R., Al-Awadhi, N., 1998. Bioremediation of damaged desert environment using the windrow soil profile system in Kuwait. Environmental International 24(1/2), 175-180.
19. Alexandar, M., 2000. Aging, bioavailability and overestimation of risk from environmental pollutants. Environmental Science and Technology, 34(20), 4259-4265.
20. Ali, A., Guo, D., Mahar, A., Wang, P., Shen, F., Li, R., Zhang, Z., 2017. Mycoremediation of potentially toxic trace elements—a biological tool for soil cleanup: A review. Pedosphere 27(2), 205-222.
21. Aljuboury, D.A.D.A., Palaniandy, P., Abdul Aziz, H.B., Ferroz, S., 2017. Treatment of petroleum wastewater by conventional and new technologies – A review. Global NEST Journal, Vol 19.
22. Al-Majed, A.A., Adebayo, A.R., Hossain, M.E., 2012. A sustainable approach to controlling oil spills. J. Environ. Manag. 113, 213–227.
23. Alshawabkeh, A.N., 2001. Basics and application of electrokinetic remediation. Handouts prepared for a short course, in Handouts Prepared for a Short Course. Federal University of Rio de Janeiro: Rio de Janeiro, 95.
24. Al-Zubaidi, I., Al-Tamimi, A., 2018. Soil remediation from lubricating oil. Environmental Technology & Innovation 9, 151-159.
25. Amro, M.M., 2004. Treatment techniques of oil-contaminated soil and water aquifers, International Conf. on Water Resources & Arid Environment, 1-11.
26. Anderson, A., Mitchell, P., 2003. Treatment of mercury-contaminated soil, mine waste and sludge using silica micro-encapsulation. TMS Annual Meeting, Extraction and Processing Division, Mar 2–6 2003, San Diego, CA, pp. 265–274.
27. Anderson, C. and Juday, G., 2016. Mycoremediation of petroleum: A literature review. Journal of Environmental Science and Engineering A5, 397-405.
28. Anthony, E.J and Wang, J., 2006. Pilot plant investigations of thermal remediation of tar-contaminated soil and oil contaminated gravel. CANMET Energy Technology Centre-Ottawa (CETC-O), Natural Resources Canada, 1 Haanel Dr., Ottawa, Ontario, K1A 1M1 Canada.
29. Arnold, C. W., Parfitt, D. G., & Kaltreider, M., 2007. Phytovolatilization of oxygenated gasoline-impacted groundwater at an underground storage tank site via conifers. International Journal of Phytoremediation 9, 53–69.
30. Artiola, J., Pepper, I.L., Brusseau, M.L., 2004. Environmental monitoring and characterization. Elsevier Science and Technology Books.
31. Asgari, A.R., Nabizadeh, R., Mahvi, A.H., Nasseri, S., Dehghani, M.H., Nazmara, S., Yaghmaeian, K., 2017. Remediation of total petroleum hydrocarbons using combined in-vessel composting and oxidation by activated persulfate. Global J. Environ. Sci. Manage., 3(4), 273-384.
32. Asghar, H.N., Rafique, H.M., Zahir, Z.A., Khan, M.Y., Akhtar, M.J., Naveed, M., Saleem M., 2016. Petroleum hydrocarbons-contaminated coils: Remediation approaches. In: Hakeem K., Akhtar J., Sabir M. (eds) Soil Science: Agricultural and Environmental Prospective. Springer, Cham.
33. Ashokkumar, M., 2011. The characterization of acoustic cavitation bubbles- An overview. Ultrasonics Sonochemistry 18, 864-872.

34. Ashrafizadeh, S.N., Motaee, E., Hoshyaargar, V., 2012. Emulsification of heavy crude oil in water by natural surfactants. Journal of Petroleum Science and Engineering 86-87, 137-143.
35. Atagana, H.I., 2008. Compost bioremediation of hydrocarbon-contaminated soil inoculated with organic manure. African Journal of Biotechnology 7(10), 1516-1525.
36. Atlas, R.M., 1981. Microbial degradation of petroleum hydrocarbons: An environmental perspective. Microbiological Reviews 45(1), 180-209.
37. ATSDR, 1999. Toxicological profile for total petroleum hydrocarbons (TPH). Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service Atlanta, GA, USA.
38. ATSDR, 2011. Total Petroleum Hydrocarbons. Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, Public Health Service Atlanta, GA, USA.
39. Australian and New Zealand Environment and Conservation Council (ANZECC), 1999. Guidelines for the assessment of non-site containment of contaminated soil.
40. Azeez, O.M., Anigbogu, C.N., Akhigbe, R.E., Saka, W.A., 2015. Cardiotoxicity induced by inhalation of petroleum products. Journal of African Association of Physiological Sciences. 3(1), 14-17.
41. Azizi, A.B., Liew, K.Y., Noor, Z.M., Abdullah, N., 2013. Vermiremediation and mycoremediation of polycyclic aromatic hydrocarbons in soil and sewage sludge mixture: a comparative study. Inter J Environ. Sci. Dev. 4(5), 565 – 568.
42. Azubuike, C.C., Chikere, C.B., Okpokwasili, G.C., 2016. Bioremediation techniques – classification based on site of application: principles, advantages, limitations and prospects. World J. Microbiol. Biotechnol. 32(11), 180.
43. Baker, R.S., Kuhlman, M., 2002. A description of the mechanisms of in-situ thermal destruction (ISTD) reactions. In: Al-Ekabi H, (ed.) Current practices in oxidation and reduction technologies for soil and groundwater: Proceedings of the 2nd International Conference on Oxidation and Reduction Technologies for Soil and Groundwater, Toronto, Canada.
44. Ballesteros, S., Rincón, J.M., Rincón-Mora, B., Jordán, M.M., 2016. Vitrification of urban soil contamination by hexavalent chromium. Journal of Geochemical Exploration.
45. Ba-Naimoon, M.S., Hamid, A.M., 2016. Stabilization/solidification (S/S) technique and its applications in Saudi Arabia. International Journal of Environment and Sustainability 5(1): 46-50.
46. Banaszkiewicz, K., Marcinkowski, T., 2017. Use of cement-fly ash-based stabilization techniques for the treatment of waste containing aromatic contaminants. E3S Web of Conferences 22, 000009.
47. Banerji, S.K., 1995. Bioremediation of soils contaminated with petroleum hydrocarbons using bio-slurry reactors. Installation Restoration Research Programe. Miscallaneous Paper IRRP-95-2.
48. Bansal, R.C., Goyal, M., 2005. Activated Carbon Adsorption. (First ed.) Boca Raton, Fla. CRC Press.
49. Barac, T., Weyens, N., Oeyen, L., Taghavi, S., van der Lelie, D., Dubin, D., Spliet, M., & Vangronsveld, J., 2009. Field note: Hydraulic containment of BTEX plume using poplar trees. International Journal of Phytoremediation 11, 416–424.

50. Barakat, A.O., Quian, Yaorong, Kim, Moonkoo, and Kennicutt, M.C., 2001, Chemical characterization of naturally weathered oil residues in arid terrestrial environment in Al-Alamein, Egypt: Environment International, 27(4), 291-310.
51. Barnes, D.L., Laderach, S.R., Showes, C., 2002. Treatment of petroleum contaminated soil in cold, wet, remote regions. USDA Forest Service Technology and Development Program Missoula, MT, USA.
52. Basta, N.T., McGowen, S.L., 2004. Evaluation of chemical immobilization treatments for reducing heavy metals transport in a smelter-contaminated soil. Environmental Pollution 127, 73-82.
53. Bates, E., Hills, C., 2015. Stabilization and solidification of contaminated soil and waste: a manual of practice. USEPA.
54. Bejarano, A.C. and Michel, J., 2010. Large-scale risk assessment of polycyclic aromatic hydrocarbons in shoreline sediments from Saudi Arabia: environmental legacy after twelve years of the gulf war oil spill, Environmental Pollution, 158(5), 1561–1569.
55. Bell, R. M., 1992. Higher plant accumulation of organic pollutants from Soils. Risk Reduction Engineering Laboratory, Cincinnati, OH. EPA/600/R-92/138.
56. Belousova, N., Baryshnikova, L., Shkidchneko, A., 2001. Selection of microorganisms capable of degrading petroleum and its products at low temperatures. Applied Biochemistry and Microbiology 38, 437-440.
57. Benyahia, F., and Embaby A.S., 2016. Bioremediation of crude oil contaminated desert soil: effect of biostimulation, bioaugmentation and bioavailability in biopile treatment systems. Int. J. Environ. Res. Public Health 13(2), 219.
58. Berg, E., 2017. Adsorption of organic and inorganic compounds on activated carbon and biochar. Dissertation, UMEA Universitet.
59. Besha, A.T., Bekele, D.N., Naidu, R., Chadalavada, S., 2018. Recent advances in surfactant-enhanced in-situ chemical oxidation for the remediation of non-aqueous phase liquid contaminated soils and aquifers. Environmental Technology & Innovation 9, 303-322.
60. Beyke, G., Fleming, D., 2005. In situ thermal remediation of DNAPL and LNAPL using electrical resistance heating. Remediation Journal 15(3),
61. Bhatnagar, S., Kumari, R., 2013. Bioremediation: a sustainable tool for environmental management – a review. Annual Review and Research in Biology 3(4), 974-993.
62. Bientinesi, M., Scali, C., Petarca, L., 2015. Radio frequency heating for oil recovery and soil remediation. IFAC ADCHEM 2015, Whistler, Bristish Columbia, Canada.
63. Bikoko, T.G.L.J., Okonta, F.N., 2016. Binder systems for the stabilization/solidification of contaminated soils- a review. Electronic Journal of Geotechnical Engineering, 21.25, 9927-9966.
64. Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B., Scheckel, K., 2014. Remediation of heavy metalloids contaminated soils – to mobilize or immobilize. Journal of Hazardous Materials 266, 141-166.
65. Boopathy, R., 2000. Factors limiting bioremediation technologies. Bioresource Technology 74, 63-67.
66. Boulakradeche, M.O., Akretche, D.E., Cameselle, C., Hamidi, N., 2015. Enhanced electrokinetic remediation of hydrophobic organics contaminated soils by the combination of non-ionic and ionic surfactants. Electrochimica Acta 174, 1057-1066.

67. Bradshaw, S.M., van Wyk, E.J., de Swardt, J.B., 1998. Microwave heating principles and the application to the regeneration of granular activated carbon. The Journal of the South African Institute of Mining and Metallurgy 201-212.
68. Brassington, K.J., Hough, R.L., Paton, G.I., Semple, K.T., Risdon, G., Crossley, J., Hay, I., Askari, K., Pollard, S.J.T., 2007. Weathered hydrocarbon wastes: a risk management primer. Crit. Rev. Environ. Sci. Technol. 37, 199-232.
69. Bretti, L.L., 2002. Soil remediation by supercritical CO2 extraction process performance and cost analysis. Master Thesis, Royal Institute of Technology, Stockholm, Sweden.
70. Brown, D.M., Okoro, S., Van Gils, J., Van Spanning, R., Bonte, M., Hutchings, T., Linden, O., Egbuche, U., Bruun, K.B., Smith, J.W.N., 2017. Comparison of landfarming amendments to improve bioremediation of petroleum hydrocarbons in Niger Delta soils. Sci. Total Environ. 596-597, 284-292.
71. Bucala, V., Saito, H., Howard, J.B., Peters, W.A., 1994. Thermal treatment of fuel oil contaminated soils under rapid heating conditions. Environ. Sci. Technol. 28, 1801–1807.
72. Bucheli, T.D., Gustafsson, O., 2000. Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. Environmental Science and Technology 34, 5144-5151.
73. Busamra, A.A.M., 2014. Treatment of oil sludge by supercritical water oxidation (SCWO). Master Thesis, College of Science, United Arab Emirate University (UAEU).
74. Byström, A., Hirtz, M., 2002. Phytoremediation of petroleum hydrocarbon-contaminated soils with *Salix viminalis*. Doctoral Thesis, Department of Water Environmental and Transport, Chalmers University of Technology, Göteborg, Sweden.
75. Cai, D., Yang, X., Wang, S., Chao, Y., Morel, J.L., Qiu, R., 2017. Effects of dissolved organic matter derived from forest leaf litter on biodegradation of phenanthrene in aqueous phase. J. Hazard. Mater. 324, 516–525.
76. Cajaraville, M.P., Marigomez, J.A., and Angulo, E., 1991. Automated measurement of lysosomal structure alterations in oocytes of mussels exposed to petroleum hydrocarbons. Archives of Environmental Contamination and Toxicology 21, 395-400.
77. Camenzuli, D., Freidman, B.L., 2015. On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in the Antarctic and Artic. Polar Research 34, 24492.
78. Camenzuli, D., Gore, D.B., 2013. Immobilization and encapsulation of contaminants using silica treatments: A review. Remediation Journal, 34(1), 49-67.
79. Cameselle, C., Gouveia, S., 2018. Electrokinetic remediation for the removal of organic contaminants in soils. In: Jaffrezic-Renault, N., Mousty, C., (eds), Environmental Electrochemistry. Current Opinion in Electrochemistry 11, 41-47.
80. Carr, A.G., Class, C.A., Lai, L., Kida, Y., Monrose, T., Green, W.H., 2015. Supercritical water treatment of crude oil and hexylbenzene: An experimental and mechanistic study on alkylbenzene decomposition. Energy & Fuel. American Chemical Society 29, 5290-5302.
81. Cartmill, A.D., Cartmill, D.L., Alarcón, A., 2014. Controlled release fertilizer increased phytoremediation of petroleum-contaminated sandy soil. Int. J. Phytoremediation 16, 285–301.
82. Castelo-Grande, T., Barbosa, D., 2003. Soil decontamination by supercritical extraction. Electronic Journal of Environmental, Agricultural and Food Chemistry 2(2), 331-226.

83. Chachina, S.B., Voronkova, N.A., Baklanova, O.N., 2016. Biological remediation of the petroleum and diesel contaminated soil with earthworms *Eisenia fetida*. Procedia Engineering 152, 122-133.
84. Chaillan, F., Le Flèche, A., Bury, E., Phantavong, Y., Grimont, P., Saliot, A., Oudot, J., 2004, Identification and biodegradation potential of tropical aerobic hydrocarbon-degrading microorganisms. Research in Microbiology, 155, 587–595.
85. Chang, K.S., Lo, W.H., Lin, W.M., Wen, J.X., Yang, S.C., Huang, C.J., Hsieh, H.Y., 2016. Microwave-assisted thermal remediation of diesel contaminated soil. Engineering Journal 20(4)
86. Chen, K.F., Chang, Y.C., Chiou, W.T., 2015. Remediation of diesel-contaminated soil using *in situ* chemical oxidation (ISCO) and the effects of common oxidants on the indigenous microbial community: a comparative study. J Chem Technol Biotechnol. 91, 1877-1888.
87. Choi, P.K., 2017. Sonoluminescence and acoustic cavitation. Japanese Journal of Applied Physics 56, 07 JAO1.
88. Chrisman, E., Lima, V., Menechini, P., 2012. Asphaltenes – problems and solutions in E and P of Brazilian crude oil. In: Abdel-Raouf, M.E., (Ed.). Crude oil emulsion – composition stability and characterisation. INTECH, Rejeka, Croatia.
89. Clark, R.B., 1999. Marine pollution. Oxford University press, Fourth edition, pp 161.
90. Clay, S.L., 2014. Identifying the fate of petroleum hydrocarbons released into the environment and their potential biodegradation using stable carbon isotopes and microbial lipid analysis. Dissertation, McMaster University.
91. Cook, R.L., Hesterberg, D., 2013. Comparison of trees and grasses for rhizoremediation of petroleum hydrocarbons. Int. J. Phytoremediation 15, 844–860.
92. Costa, A.S., Romao, L.P., Araujo, B.R., Lucas, S.C., Maciel, S.T., Wisniewski Jr., A., Alexandre, M.R., 2012. Environmental strategies to remove volatile aromatic fractions (BTEX) from petroleum industry wastewater using biomass. Bioresour. Technol. 105, 31–39.
93. Coste, A., Micle, V., Băbuţ, C.S., 2013. Study on the in-situ bioremediation techniques applicable to soil contaminated with petroleum products. ProEnvironment 6, 463-468.
94. Coulon, F., Al Awadi, M., Cowie, W., Mardlin, D., Pollard, S., Cunningham, C., Risdon, G., Arthur, P., Semple, K.T., Paton, G.I., 2010. When is a soil remediated? Comparison of biopiled and windrowed soils contaminated with bunker-fuel in a full-scale trial. Environ Pollut 158, 3032–3040.
95. Covino, S., D'Annibale, A., Stazi, S.R., Cajthami, T., Cvancarova, M., Stella, T., Petruccioli, M., 2015. Assessment of degradation potential of aliphatic hydrocarbons by autochthonous filamentous fungi from a historically polluted clay soil. Sci. Total Environ. 505, 545-554.
96. Cristaldi, A., Conti, G.O., Jho, E.H., Zuccarello, P., Grasso, A., Copat, C., Ferrante, M., 2017. Phytoremediation of contaminated soils by heavy metals and PAHs. A brief review. Environmental Technology & Innovation 8, 309-326.
97. Cuevas, C.L., Hernández, B.E., 2011. Use of microwaves in the pharmaceutical industry. Rev Mex Ciencias Farm 42(Número),6–25.
98. Dabke, S.V., 2013. Vermiremediation of heavy metal-contaminated soil. Blacksmith Institute J. Hlth Poll. 3(4), 4-10.

99. Dadrasnia, A., Agamuthu, P., 2014. Biostimulation and monitoring of diesel fuel polluted soil amended with biowaste. Pet. Sci. Technol. 32, 2822–2828.
100. Dadrasnia, A., Shahsavari, N., and Emenike, C.U., 2013. Remediation of contaminated sites. Hydrocarbon, INTECH, Hydrocarbon. 4, 66-82.
101. Daghio, M., Aulenta, F., Vaiopoulou, E., Franzetti, A., Arends, J.B.A., Sherry, A., et al., 2017. Electrobioremediation of oil spills. Water Res. 114, 351–370.
102. Damgard, I., 2012. Enhanced reductive dechlorination in clay fill contaminated with chlorinated solvents., PhD Thesis. DTU Environment
103. Danielle, C., Freidman, B.L., 2015. On-site and in situ remediation technologies applicable to petroleum hydrocarbon contaminated sites in the Antarctic and Arctic, Polar Research, 34:1.
104. Das, N., and Chandran, P., 2011. Microbial degradation of petroleum hydrocarbon contaminants: An overview. Sage-Hindawi, Biotechnology Research International. Volume 2011, Article ID 941810, 13 pages. doi:10.4061/2011/941810.
105. Demčák, S., Bálintová, M., 2015. Overview of chosen techniques and methods for soils remediation. In: Zborník recenzovaných vedeckých prác ÚEI. - Košice : TU, S. 95-102.
106. Deppe, U., Richnow, H.H., Michaelis, W., Antranikian, G., 2005. Degradation of crude oil by an arctic microbial consortium. Extremophiles 9 (6), 461–470.
107. Derakhshan, N.Z., Jung, M.C., Kim, K.H., 2017. Remediation of soils contaminated with heavy metals with an emphasis on immobilization technology. Environmental Geochemistry and Health, 1-27.
108. Dias, R.L., Ruberto, L., Calabró, A., Balbo, A.L., Del Panno, M.T., Mac Cormack, W.P. 2015. Hydrocarbon removal and bacterial community structure in on-site bio stimulated biopile systems designed for bioremediation of diesel-contaminated Antarctic soil. Polar Biol. 38, 677–687.
109. Dindar E., Şağban F.O.T., Başkaya H.S., 2013. Bioremediation of petroleum contaminated soil. J. Biol. Environ. Sci. 7, (19), 39.
110. Driscoll, T.P., Barber, J.B., Chandran, K., Constable, S., Darnell, C., DiMenna, R., Gaines, B., Goodman, A., Hlavek, R., Johns, F.J., Jones, T.S., Kemp, G., Kim, B., Krill, W.P., Maillacheruvu, K., Millano, E.F., Nichols, C., Parham, G., Philbrook, D., Severin, B.F., Shamas, J., Shamskhorzani, R., Solvie, J., Venkatasubbiah, V., Wirtz, R., WongChong, G., Yeh, B., Young, J., 2008. Industrial wastewater management, treatment, and disposal. WEF manual of practice no. FD-3rd. Mcgraw-Hill, New York, 474–489.
111. Dwivedi, S., 2012. Bioremediation of heavy metals by algae: current and future perspective. J Adv Lab Res Biol. 3(3), 195-199.
112. Dzionek, A., Wojcieszyńska, D., Guzik, U., 2016. Natural carriers in bioremediation: A review. Electronic Journal of Biotechnology 23, 28–36.
113. Ekperusi, O.A., Aigbodion, F.I., 2015. Bioremediation of petroleum hydrocarbons from crude oil contaminated soil with the earthworm: *Hyperiodrilus africanus*. 3 Biotech 5:957.
114. El-Sheekh, M.M., Hamouda, R.A., Nizam, A.A., 2013. Biodegradation of crude oil by *Scenedesmus obliquus* and *Chlorella vulgaris* growing under heterotrophic conditions. Int. Biodeterior. Biodegrad. 82, 67–72.
115. ENGEO 2015. Soil management plan. SummerHill Apartment Communities, Rollins Road -Carolan Avenue Parcels, Burlingame, California.

116. Eren, Z., Ultrasound as a basic and auxiliary process for dye remediation: A review. Journal of Environmental Management 104, 127-141.
117. Esbaugh, A.J., Mager, E.M., Stieglitz, J.D., Hoenig, R., Brown, T.L., French, B.L., Linbo, T.L., Lay, C., Forth, H., Scholz, N.L., John, P., Incardona, J.P., Morris, J.M., Benetti, D.D., Grosell, M., 2016. The effects of weathering and chemical dispersion on Deepwater Horizon crude oil toxicity to mahi-mahi (Coryphaena hippurus) early life stages. Science of the Total Environment 543, 644-651
118. Fabbricino, M., Ferraro, A., Luongo, V., Pontoni, L., Race, M., 2018. Soil washing optimization, recycling of the solution, and ecotoxicity assessment for the remediation of Pb-contaminated sites using EDDS. Sustainability 10, 636.
119. Falciglia, P.P., Bonifacio, A., Vagliasindi, F.G.A., 2016. An overview of microwave heating application for hydrocarbon contaminated soil and groundwater remediation. Oil Gas Res 2, 110.
120. Falciglia, P.P., Roccaro, P., Bonanno, L., De-Guidi, G., Vagliasindi, F.G.A., Romano, S., 2018. A review on the microwave heating as a sustainable technique for environmental remediation/detoxification applications. Renewable and Sustainable Energy Reviews 95, 147-170.
121. Falciglia, P.P., Urso, G., Vagliasindi, F.G.A., 2013. Microwave heating remediation of soils contaminated with diesel fuel. J. Soils Sediments 13, 1396-1407.
122. Fallgren, P.H and Jin, S. 2008. Biodegradation of petroleum compounds in soil by a solid-phase circulating bioreactor with poultry manure amendments. Journal of Environmental Science and Health Part A, 43, 125-131.
123. Fathi, A.A., Azooz, M.M., Al-Fredan, M.A., 2013. Phycoremediation and the potential of sustainable algal biofuel production using wastewater. Am J Appl Sci. 10(2), 189-194.
124. Finžgar, N., Kos, B., Leštan, D., 2006. Bioavailability and motility of Pb after soil treatment with different remediation methods, Plant, Soil and Environment 52(1), 25-34.
125. Fiocco, R.J., Lewis, A., 1999. Oil spill dispersants. Pure and Applied Chemistry 71(1), 27–42.
126. Flores, R., Blass, G., Dominguez, V., 2007. Soil remediation by an advanced oxidative method assisted with ultrasonic energy. J Hazardous Mater 140, 399-402.
127. Fox, R.D., 1996. Physical/chemical treatment of organically contaminated soils and sediments. Air & Waste Manage. Assoc. 46, 391-413.
128. Fritsche, W. and Hofrichter, M., 2000. Aerobic degradation by microorganisms, in Environmental Processes – Soil decontamination, Klein, J., Ed., Wiley-Vch, Weinheim, Germany, 146-155.
129. Galdames, A., Mendoza, A., Orueta, M., deSoto-Gracia, I.S., Sánchez, M., Virto, I., Vilas, J.L. 2017. Development of new remediation technologies for contaminated soils based on the application of zero-valent iron nanoparticles and bioremediation with compost. Resource-Efficient Technologies 3(3), 166-176.
130. Gani, P., Sunar, N.M., Matias-Peralta, P., Latiff, A.A., Parjo, U.K., Ab. Razak, A.R., 2015. Phycoremediation of wastewaters and potential hydrocarbon from microalgae: A review. Advances in Environmental Biology 9(20), 1-8.
131. Garg, A.P., Gandotra, S., Mukerji, K.G., Pugh, G.J.F., 1985. Ecology of keratinophilic fungi. Proc. Indian Acad. Sci. (Plant Sci.), 149-163.
132. Gatliff, E. G., 1994. Vegetative remediation process offers advantages over traditional pump-and-treat technologies. Remed. Summer 4(3), 343-352.

133. Gennadiev, A., Yu, N., Pikovskii, I., Tsibart, A.S., Smirnova, M.A., 2015. Hydrocarbons in Soils: Origin, Composition, and Behavior (Review). Eur. Soil Sci. 48, 1076-1089.
134. Gerber, M. A., Fayer, M.J., 1994. *In Situ* Remediation Integrated Program Evaluation and Assessment of Containment Technology. Washington, DC: U.S. Dept. of Energy, Office of Environmental Management, Office of Technology Development
135. Glaze, W. H.; Kenneke, J. F.; and Ferry, J. L., 1993. Chlorinated byproducts from the TiO_2-mediated photodegradation of trichloroethylene and tetrachloroethylene in water, Environmental Science & Technology 27(1), 177-184.
136. Godheja, J., Shekhar, S.K., Siddiqui, S.A., Modi, D.R., 2016. Xenobiotic compounds present in soil and water: A review on remediation strategies. J. Environ. Anal. Toxicol. 6, 5.
137. Godheja, J., Shekhar, S.K., Siddiqui, S.A., Modi, D.R., 2016. Xenobiotic compounds present in soil and water: A review on remediation strategies. Journal of Environmental & Analytical Toxicology 6, 392.
138. Gomez, F., Sartaj, M., 2014. Optimization of field scale biopiles for bioremediation of petroleum hydrocarbon contaminated soil at low temperature conditions by response surface methodology (RSM) Int Biodeterior Biodegradation 89, 103–109
139. Gouda, A.H., El-Gendy, A.S., Abd El-Razek, T.M., El-Kassas, H.I., 2016. Evaluation of phytoremediation and bioremediation for sandy soil contaminated with petroleum hydrocarbons. International Journal of Environmental Science and Development 7(7).
140. Grant, G.P., Major, D., Scholes, G.C., Horst, J., Hill, S., Klemmer, M.R., Couch, J.N., 2016. Smoldering combustion (STAR) for the treatment of contaminated soils: examining limitations and defining success. Remediation. The Journal of Environmental Cleanup Costs, Technology and Techniques 26(3).
141. Greipsson, S., 2011. Phytoremediation. Nature Education Knowledge 3(10), 7.
142. Guarino, C., Spada, V., Sciarrillo, R., 2017. Assessment of three approaches of bioremediation (natural attenuation, landfarming and bioaugmentation – assisted landfarming) for a petroleum hydrocarbons contaminated soil. Chemosphere 170, 10-16.
143. Gultekin, I., Tezcanli-Guyer, G., Ince, N.H., 2009. Sonochemical decay of CI Acid Orange 8: effects of CCl4 and t-butyl alcohol. Ultrasonics Sonochemistry 16(4), 577-581.
144. Gutiérrez, T., 2017. Bio-dispersants: do they have a future to combat marine oil spills? Mar Microbiol. 1(1), 9-10.
145. Gutzkow, K.B., 2015. Genetoxicity, mutagenicity and carcinogenicity and Reach. ICAW. Norwegian Institute of Public Health.
146. Haggblom, M.M., Ahn, Y-B., Fennell, D.E., Kerkhof, L.J., Rhee, S-K., 2003. Anaerobic dehalogenation of organohalide contaminants in the marine environment. Adv Appl Microbiol 53,61-84.
147. Hamzah, A., Phan, C.W., Abu Bakar , N.F., Wong, K.K., 2013. Biodegradation of crude oil by constructed bacterial consortia and the constituent single bacteria isolated from Malaysia, Bioremediation Journal, 17(1), 1-10.
148. Haque, M.M., Bahnemann, D., Muneer, M., 2012. Photocatalytic degradation of organic pollutants: mechanisms and kinetics. In: Puzyn, T. (ed), Organic pollutants ten years after Stockholm convention – environmental and analytical update. InTech, 293-326.
149. Hara, J., 2012. Chemical degradation of chlorinated organic pollutants for in situ remediation and evaluation of natural attenuation. Organic Pollutants Ten Years After the

Stockholm Convention Environmental and Analytical Update, Dr. Tomasz Puzyn (Ed.), INTECH Chapter 14, 345-364.

150. Harvey, S., Elashvili, I., Valdes, J.J., Kamely, D., Chakrabarty, A.M., 1990. Enhanced removal of Exxon Valdez spilled oil from Alaskan gravel by a microbial surfactant. Biotechnology (NY) 8(3), 228-230.
151. Hass, H., Schäfers, P., 2006. Application of ground freezing for underground construction in soft ground. In Geotechnical Aspects of Underground Construction in Soft Ground. London: Taylor & Francis.
152. Hassan, I.A., 2016. Electrokinetic enhanced bioremediation of soils contaminated with petroleum hydrocarbons. Electronic Thesis and Dissertation Repository. 3693.
153. Hassanshahian, M., Cappello, S., 2013. Crude Oil Biodegradation in the Marine Environments, Biodegradation - Engineering and Technology, Dr. Rolando Chamy (Ed.), InTech, DOI: 10.5772/55554.
154. Hazen, T.C. 2010. Biostimulation, Timmis, K.N. (ed.), Handbook of hydrocarbon and lipid microbiology, Springer-Verlag Berlin Heidelberg.
155. He, P.J., Mao, B., Shen, C.M., Shao, L.M., Lee, D.J., Chang, J.S., 2013. Cultivation of *Chlorella vulgaris* on wastewater containing high levels of ammonia for biodiesel production. Bioresour. Technol. 129, 177–181
156. Hellström, A., 2004. Uptake of organic pollutants in plants. Department of Environmental and Assessments, Swidish University of Agricultural Sciences, Uppsala.
157. Hentati, O., Lachhab, R., Ayadi, M., Ksibi, M., 2013. Toxicity assessment for petroleum-contaminated soil using terrestrial invertebrates and plant bioassays. Environ. Monit. Assess. 185:2989-2998.
158. Hobson, A.M., Frederickson, J., Dise, N.B., 2005. CH_4 and N_2O from mechanically turned windrow and vermincomposting systems following in-vessel pre-treatment. Waste Manag. 25, 345-352.
159. Hoff, R.Z., 1993. Bioremediation: an overview of its development and use for oil spill cleanup. Mar. Pollut. Bull. 26, 476–481.
160. Hong, M., Farmayan, W., Dortch, I., Chiang, C., McMillan, S., & Schnoor, J., 2001. Phytoremediation of MTBE from a groundwater plume. Environmental Science & Technology, 35, 1231–1239.
161. Hreniuc, M., Coman, M., Cioruța, B., 2015. Consideration regarding the soil pollution with oil products in Sacel-Maramures. International Conference of scientific paper AFASES. Brasov. pp. 28-30.
162. Hu, G., 2016. Development of novel oil recovery methods for petroleum refinery oily sludge treatment. Ph.D Dissertation. University of Northern British Columbia.
163. Hu, G., Li, J., Huang, S., Li, Y., 2016. Oil recovery from petroleum sludge through ultrasonic assisted solvent extraction. Toxic/Hazardous Substances and Environmental Engineering, 51(11): 921-929.
164. Hubler, J., Metz, K., 2013. Soil washing. Web-based class project on geoenvironmental remediation. CEE 549: Geoenvironmental Engineering.
165. Huling, S.G., Pivetz, B.E., 2006. In situ chemical oxidation. Engineering Issue. United States Environmental Protection Agency.
166. Huon, G., Simpson, T., Holzer, F., Maini, G., Will, F., Kopinke, F.D., Roland, U., 2012. *In situ* radio frequency heating for soil remediation at a former service station: Case study and general aspect. Chem. Eng. Technol. 35(8), 1534-1544.

167. Hussain, I., Puschenreiter, M., Gerhard, S., Schöftner, P., Yousaf, S., Wang, A., Syed, J.H., Reichenauer, T.G., 2018. Rhizoremediation of petroleum hydrocarbon contaminated soil: Improvement opportunities and field applications. Environmental and Experimental Botany 147, 202-219.
168. Ibrahim, R., 2009. Contaminated land management and control guidelines No. 3: Remediation of contaminated sites. Jabatan Alam Sekitar (Department of Environment) Malaysia.
169. IPIECA-IOGP. 2015. Dispersants: surface application. Good practice guidelines for incident management and emergency response personnel. International Association of Oil and Gas Producers (IOGP) Report 532.
170. Iqbal, M., Ali, Akbar, A., Nahyoon, N.A., Majeed, A., Pothu, R., Phulpoto, S., Thebo, K.H., 2019. Photocatalytic degradation of organic pollutants with nano-sized cadmium sulfide. Materials Science for Energy Technologies 2, 41-45.
171. Issaka, S.A., Nour, A.H., Yunus, R.M., 2015. Review on the fundamental aspects of petroleum oil emulsions and techniques of de-emulsification. Journal of Petroleum and Environmental Biotechnology 6, 2
172. Istrate, I.A., Cocârtă, D.M., Wu Z., Stoian, M.A., 2018. Minimizing the health risks from hydrocarbon-contaminated soils by using electric-field based treatment for soil remediation. Sustainability 10, 253.
173. ITOPF. 2011. Technical information paper. The International Tanker Owners Pollution Federation.
174. ITRC, 2000. In situ oxidation. Technical and Regulatory Guidance. Interstate Technology and Regulatory Cooperation Work Group.
175. Iturbe, R., López, J., 2015. Bioremediation for a Soil Contaminated with Hydrocarbons. J Pet Environ Biotechnol 6, 208.
176. Ivshina, I.B., Kuyukina, M.S., Krivoruchko, A.V., Elkin, A.A., Makarov, S.O., Cunningham, C.J., Peshkur, T.A., Atlas, R.M., Philip, J.C., 2015. Oil spill problems and sustainable response strategies through new technologies. Environmental Science Process and Impact. Royal Society of Chemistry, 17, 1201-1219.
177. Iyer, R., 2001. Electrokinetic remediation. Particulate Science and Technology 19(3), 219-228.
178. Jang, K.Y., Cho, S.M., Seok, S.J., Kong, W.S., Kim, G.H., Sung, J.M., 2009. Screening of biodegradable function of indigenous lingo-degrading mushroom using dyes. Mycobiology 4, 53-61.
179. Jankaite, A., Vasarevičius, S., 2005, Remediation technologies for soils contaminated with heavy metals. Journal of Environmental Engineering and Landscape Management 13(2), 109a-113a.
180. Jesus, J.M., Danko, A.S., Fiúza, A., Borges, M.T., 2015. Phytoremediation of salt-affected soils: a review of processes, applicability, and the impact of climate change. Environ Sci. Pollut. Res. 22:6511-6525.
181. Jiang, Y., Brassington, K.J., Prpich, G., Paton, G.I., Semple, K.T., Pollard, S.J.T., Coulon, F., 2016. Insights into the biodegradation of weathered hydrocarbons in contaminated soils by bioaugmentation and nutrient stimulation. Chemosphere 161, 300-307.

Journal Pre-proof

182. Jones, D.M, Douglas, A.G., Parkes, R.J., 1983. The recognition of biodegraded petroleum–derived aromatic hydrocarbons in recent marine sediments. Marine Pollution Bulletin 14(3), 103–108.
183. Joutey, N.T., Bahafid, W., Sayel, H., El-Ghachtouli, N., 2013. Biodegradation: involved microorganisms and genetically engineered microorganisms. INTECH, Biodegradation-Life Science 11, 290-320.
184. Joye, S., MacDonald, I., 2010. Offshore oceanic impacts from the BP oil spill, Nat. Geosci. 3(7), 446.
185. Kalhor, A.X., Movafeghi, A., Mohammadi-Nassab, A.D., Abedi, E., Bahrami, A., 2017. Potential of the alga Chlorella vulgaris for biodegradation of crude oil hydrocarbons. Marine Pollution Bulletin 123, 286-290.
186. Kalmykova, Y., Moona, N., Stromvall, A-M, Bjorklund, K., 2014. Sorption and degradation of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, alkylphenols, bisphonel A and phthalates in landfill leachate using sand, activated carbon and peat filters. Water Research 56, 246-257.
187. Kanel, S.R., Greeneche, J.M., Choi, H., 2006. Arsenic (V) removal from groundwater using nanoscale zerovalent iron as a colloidal reactive barrier material. Environ Sci Technol. 40, 2045–2050.
188. Kang, W.H., Cheong, J.G., Kim, K., Chae, H., Chang, C.H., 2012. Restoration of petroleum contaminated soils by field scale soil washing system. International Conference on Environmental Science and Technology 30
189. Kao, C.M., Chen, C.Y., Chen, S.C., Chien, H.Y., Chen, Y.L., 2007. Application of in situ biosparging to remediate a petroleum hydrocarbon spill spite: Field and microbial evaluation. Chemospher 70, 1492-1499.
190. Karanfil, T., Kilduff, J.E., 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds. one priority pollutants. Environ. Sci. Technol. 33(18), 3217-3224.
191. Karthikeyan, R., Bhandari, A., 2001. Anaerobic biotransformation of aromatic and polycyclic aromatic hydrocarbons in soil microcosms: A review. Journal of Hazardous Substance Research 3, 3-19.
192. Kastanek, F., Topka, P., Soukup, K., Maleterova, Y., Demnerova, K., Kastanek, Solcova, O., 2006. Remediation of contaminated soils by thermal desorption; effect of benzoyl peroxide addition. Journal of Cleaner Production. Vol. 125 309-313.
193. Kästner, M., Miltner, A., 2016. Application of compost for effective bioremediation of organic contaminants and pollutants in soil. Appl. Microbiol. Biotechnol. 100, 3433–3449.
194. Keramitsoglou I., Certalis C., Kassomenos P., 2003. Decision support system for managing oil spill events. Environmental. Management. 32, (2), 290.
195. Khan, F.I., Husain, T., Hejazi, R., 2004. An overview and analysis of site remediation technologies. Journal of Environmental Management 71, 95-122.
196. Khan, M.M., Adil, S.F., Al-Mayouf, A., 2015. Metal oxides as photocatalysts. J Saudi Chem Soc 19(5), 462–464.
197. Khayyat, S., Roselin, L.S., 2017. Photocatalytic degradation of benzothiophene and dibenzothiophene using supported gold nanoparticle. Journal of Saudi Chemical Society. 21, 349-357.

198. Khodadadi, A., Ganjidoust, H., Seyed-Razavi, S.N., 2012. Treatment of crude oil contaminated soil using biosurfactants. Journal of Petroleum and Gas Engineering 3(6), 92-98.
199. Kim, J., Lee, A.H., Chang, W., 2018. Enhanced bioremediation of nutrient-amended petroleum hydrocarbon contaminated soil over a cold climate winter: The rate and extent of hydrocarbon biodegradation and microbial response in a pilot-scale biopile subjected to natural seasonal freeze-thaw temperatures. Science of the Total Environment 612, 903-913.
200. Kim, S-O., Lee, K-Y, Kim, K-W., 2015. Fundamental of electrokinetics. In: Bundschuh, J., Hollander, H.M., Ma, L.Q., (eds). In-situ remediation of arsenic contaminated sites. Arsenic in the Environment 6.
201. Kim, Y., Wang M., 2003. Effect of ultrasound on oil removal from soils, Ultrasonics, 41, 539 – 542.
202. Kluck, C., Achari, G., 2004. Chemical oxidation techniques for in situ remediation of hydrocarbon impacted soils. Proceedings RemTech.
203. Koehlert, K., 2017. Activated carbon: fundamentals and new applications. Chemical Engineering, 32-40.
204. Komossa, D., Langebartels, C., Sandermann Jr., H., 1995. Metabolic processes for organic chemicals in plants. In S. Trapp and J. C. McFarlane (eds.), Plant contamination: modeling and simulation of organic chemical processes. Lewis Publishers, Boca Raton, FL.
205. Kösesakal, T., Ünal, M., Kulen, O., Memon, A., Yüksel, B., 2015. Phytoremediation of petroleum hydrocarbons by using a freshwater fern species *Azolla filiculoides* Lam, International Journal of Phytoremediation, 18(5), 467-476.
206. Kostka, J.E., Prakash, O., Overholt, W.A., Green, S.J., Freyer, G., Canion, A., Delgardio, J., Norton, N., Hazen, T.C., Huettel, M., 2011. Hydrocarbon-degrading bacteria and the bacterial community response in Gulf of Mexico beach sands impacted by the deepwater horizon oil spill. Appl. Environ. Microbiol. 77, 7962-7974.
207. Krouzek, J., Durdak, V., Hendrych, J., Masin, P., Sobek, J., Spacek, P., 2018. Pilot scale applications of microwave heating for soil remediation. Chemical Engineering and Processing: Process Intensification 130, 53-60.
208. Kuhn, E. P., Suflita, J.M., 1989. Dehalogenation of pesticides by anaerobic microorganisms in soils and groundwater - a review. pp. 111-180. In: B. L. Sawhney, B.L., Brown, K., (eds.) Reactions and movement of organic chemicals in soils. Soil Sci. Soc. America Special Publication No. 22. Soil Sci. Soc. America, Inc. Madison, WI.
209. Kulkarni, S.J., Kaware, J.P., 2013. Review on research for removal of phenol from wastewater. International Journal of Scientific and Research Publications 3(4).
210. Kuma, B., Smita, K., Flores, L.C., 2017. Plant mediated detoxification of mercury and lead. Arabian Journal of Chemistry 10, S2335-S2342.
211. Kumar, A., Tripti, Prasad, M.N.V., Maiti, S.K., Favas, P.J.C., 2018. Mycoremediation of mine site rehabilitation. Bio-Geotechnologies of Mine Site Rehabilitation. 233-260.
212. Kumar, M., Lakshmi, C.V., Khanna, S., 2008. Microbial biodiversity and in situ bioremediation of endosulfan contaminated soil. Indian J Microbiol 48:128.
213. Kumari, B., Singh, D.P., 2016. A review on multifaceted application of nanoparticles in the field of bioremediation of petroleum hydrocarbons. Ecological Engineering, 97, 98-105.

214. Kuppusamy, S., Palanisami, T., Megharaj, M., Venkateswarlu, K., Naidu, R., 2016. Ex-situ remediation technologies for environmental pollutants: A critical perspective. Reviews of environmental contamination and toxicology. 236, 117-192.
215. Kuppusamy, S., Palanisami, T., Megharaj, M., Venkateswarlu, K., Naidu, R., 2016. In-situ remediation approaches for the management of contaminated sites: A comprehensive overview. Reviews of environmental contamination and toxicology. 236, 1-116.
216. Kushwaha, D., Saha, S and Dutta, S., 2014. Enhanced biomass recovery during phycoremediation of Cr(VI) using cyanobacteria and prospect of biofuel production. Industrial & Engineering Chemistry Research 53 (51), 19754-19764
217. Kvenvolden, K.A and Cooper, C.K., 2003. Natural seepage of crude oil into the marine environment, Geo-Marine Letters, 23(3-4), 140–146.
218. Lawal, A.T., 2017. Polycyclic aromatic hydrocarbons. A review. Cogent Environmental Science. 3, 1339841.
219. Lee, K., Boufadel, M., Chen, B., Foght, J., Hodson, P., Swanson, S., Venosa, A., 2015. Expert panel report on the behaviour and environmental impacts of crude oil released into aqueous environments. Royal Society of Canada, Ottawa.
220. Li, D., Zhang, Y., Quan, X., Zhao, Y., 2009. Microwave thermal remediation of crude oil contaminated soil enhanced by carbon fibre. Journal of Environmental Sciences 21, 1290-1295.
221. Li, J., Song, X., Hu, G., Thring, R.W., 2013. Ultrasonic desorption of petroleum hydrocarbons from crude oil contaminated soils. Journal of Environmental Science and Health, Part A. Toxic/Hazardous Substances and Environmental Engineering, 48(11).
222. Li, M., Li, J.T., Sun, H.W., 2008. Decolorizing of azo dye Reactive red 24 aqueous solution using exfoliated graphite and H_2O_2 under ultrasound irradiation. Ultrasonics Sonochemistry 15 (5), 717-723.
223. Li, X., Du, Y., Wu, G., Sui, H., 2012. Solvent extraction of heavy crude oil removal from contaminated soils. Chemosphere 88(2), 245-249.
224. Lim, M.W., Lau, E.V., Poh, P.E., 2016. A comprehensive guide of remediation technologies for oil contaminated soil – present works and future directions. Marine Pollution Bulletin 109, 14-45.
225. Lin, J.J., Zhao, X.S., Liu, D., Yu, Z.G., Zhang, Y., Xu, H., 2008. The decoloration and mineralization of azo dye CI Acid Red 14 by sonochemical process: rate improvement via Fenton's reactions. Journal of Hazardous Materials 157 (2-3), 541-546.
226. Liotta, L.F., Gruttadauria, M., DiCarlo, G., Perrini, G., Librando, V., 2009. Heterogeneous catalytic degradation of phenolic substrates: catalysts activity. J Hazard Mater. 162(2-3), 5888-606.
227. Liu, J., Zhang, H., Yao, Z., Li, X., Tang, J., 2019. Thermal desorption of PCBs contaminated soil with calcium hydroxide in a rotary kiln. Chemosphere 220, 1041-1046.
228. Logeshwaran, P., Megharaj, M., Chadalavada, S., Bowman, M., Naidu, R., 2018. Petroleum hydrocarbons (PH) in groundwater aquifers: An overview of environmental fate, toxicity, microbial degradation and risk-based remediation approaches. Environmental Technology & Innovation 10, 175-193.
229. Lombi, E., Wenzel, W.W., Adriano, D.C., 1998. Soil contamination, risk reduction and remediation. Land Contamination and Reclamation 6(4)

230. Lupacchini, M., Mascitti, A., Giachi, G., Tonucci, L., D'Alessandro, N., Martinez, J., Colacino, E., 2017. Sonochemistry in non-conventional, green solvents or solvent-free reactions. Tetrahedron 73, 609-653.
231. Ma, J., Yang, Y., Dai, X., Li, C., Wang, Q., Chen, C., Yan, G., Guo, S., 2016. Bioremediation enhances the pollutant removal efficiency of soil vapour extraction (SVC) in treating petroleum drilling waste. Water Air Soil Pollution 227, 465.
232. Mahjoub, B., 2014. Plants for soil remediation. In Gaspard, S., Ncibi, M.C. (ed) Biomass for sustainable applications: pollution remediation and energy. RSC Green Chemistry 25, 106-143.
233. Mai, F. D., Chen, C. C., Chen, J. L., Liu, S. C., 2008. Photodegradation of methyl green using visible irradiation in ZnO suspensions. Determination of the reaction pathway and identification of intermediates by a high-performance liquid chromatography-photodiode array-electrospray ionization-mass spectrometry method. Journal of Chromatography A, 1189(1-2), 355-365.
234. Maletic, S.P., Dalmacija, B.D., Roncevic, S.D., 2013. Petroleum hydrocarbon biodegradability in soil – implications for bioremediation. INTECH, Hydrocarbon 3, 43-64.
235. Maletic, S.P., Dalmacija, B.D., Roncevic, S.D., Agbaba, J.R., Perovic, S.D.U., 2011. Impact of hydrocarbon type, concentration and weathering on its biodegradability in soil. J. Environ. Sci. Health, Part A 46, 1042-1049.
236. Mancera-López, M.E., Esparza-García, F., Chávez-Gómez, B., Rodríguez-Vázquez, R., Saucedo-Castañeda, G., Barrera-Cortés, J., 2008. Bioremediation of an aged hydrocarbon-contaminated soil by a combined system of biostimulation–bioaugmentation with filamentous fungi. Int. Biodeterior. Biodegrad. 61, 151–160.
237. Margesin, R., Labbe, D., Schinner, F., Greer, C.W., Whyte, L.G., 2003. Characterization of hydrocarbon-degrading microbial populations in contaminated and pristine alpine soils. Appl. Environ. Microbiol. 69 (6), 3085-3092.
238. Mason, T.J., Collings, A., Sumel, A., 2004. Sonic and ultrasonic removal of chemical contaminants from soil in laboratory and on a large scale. Ultrasonics Sonochemistry 11, 205-210.
239. Meegoda, J.N., 1999. Stabilisation/solidification of petroleum-contaminated soils with asphalt emulsion. Practice Periodical of Hazardous Toxic and Radioactive waste management 3(1), 46-55.
240. Megharaj, M., & Naidu, R., 2017. Soil and brownfield bioremediation. Microbial Biotechnology, 10(5), 1244–1249.
241. Mendez-Natera, JR, Roque, C., Zapata, K. and Otahola-Gómez, V., 2004. Effect of concentration and time of soil contamination by oil on germination of maize seeds (*Zea mays* L.) Cv. Himeca 95. Revista UDO Agrícola, 4, 66-71.
242. Menéndez, J.A., Arenillas, A., Fidalgo, B., Fernández, Y., Zubizarreta, L., Calvo, E.G., Bermúdez, J.M., 2010. Microwave heating processes involving carbon materials. Fuel Processing Technology 91, 1-8.
243. Meskar, M., 2018. Treatment of petroleum contaminated soil using supercritical fluid extraction (SFE) technology. PhD thesis, Ottawa-Carleton Institute for Civil Engineering, University of Ottawa, Canada.
244. Mirsal, I., 2008. Soil Pollution. Origin, Monitoring & remediation, second ed. Springer, Berlin Heidelberg.

245. Mishra, A.K., Kumar, G.S., 2015. Weathering of oil spill: modeling and analysis. Aquatic Procedia, 4, 435-442.
246. Mitchell, J.K., Soga, K., 2005. Fundamentals of soil behaviour, 3rd edition, John Wiley and Sons Inc., New York.
247. Mohan, D., Pittman, C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 20, 848–889.
248. Moldoveanu, S.C., 2019. Chapter 2 - Pyrolysis of Hydrocarbon. Pyrolysis of Organic Molecules (Second Edition). Applications to Health and Environmental Issues, 35-161.
249. Morselli, L., De Robertis, C., Luzi, J., Passarini, F., Vassura, I., 2008. Environmental impacts of waste incineration in a regional system (Emilia Romagna, Italy) evaluated from a life cycle perspective. J Hazard Mater. 159(2-3), 505–11.
250. Morselli, L., Setti, L., Iannuccili, A., Maly, S., Dinelli, G., Quattroni, G., 1999. Supercritical fluid extraction for the determination of petroleum hydrocarbons in soil. Journal of Chromatography A, 845, 357-363.
251. Mosavat, N., Oh, E., Chai, G., 2012. A review of electrokinetic treatment technique for improving the engineering characteristics of low permeable problematic soils. Int. J. of GEOMATE 2(2), 266-272.
252. Motamedimehr, S., Gitipour, S., Ardestani, M., 2018. Polycyclic aromatic hydrocarbons separation from oil contaminated soil using supercritical and subcritical water. Journal of Environmental Pollution and Control 1(1), 106-123
253. Moubasher, H.A., Hegazy, A.K., Mohamed, N.H., Moustafa, Y.M., Kabiel, H.F., Hamad, A.A., 2015. Phytoremediation of soils polluted with crude petroleum oil using *Bassia scoparia* and its associated rhizosphere microorganisms. Int. Biodeterior. Biodegrad. 98, 113-120.
254. Mullakaev, M.S., Vexler, G.B., Mullakaev, G.B., 2018. Sonochemical technology for separating oil sludge and oil contaminated soil. Petroleum Science and Technology, 36(8).
255. Mulligan, C.N., Gibbs, B.F., 1993. Factors influencing the economics of biosurfactants. In: Kosaric, N., (Ed.), Biosurfactants, Production, Properties, Applications. Marcel Dekker, New York, 329-371.
256. Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Remediation technologies for metal contaminated soils and groundwater: an evaluation. Engineering Geology, 193-207.
257. Mulligan, C.N., Yong, R.N., Gibbs, B.F., 2001. Surfactant enhanced remediation of contaminated soil: a review. Engineering Geology 60, 317-380.
258. Muratova, A., Hübner, T., Narula, N., Wand, H., Turkovskaya, O., Kuschk, P., Jahn, R., Merbach, W., 2003. Rhizosphere microflora of plants used for the phytoremediation of bitumen-contaminated soil. Microbiol. Res. 158, 151–161.
259. Murena, F., Gioia, F., 2009. Solvent extraction of chlorinated compounds from soils and hydrodechlorination of the extract phase. J. Hazard. Mater. 162, 661–667.
260. Mutyala, S., Fairbridge, C., Paré, J.R.J., Bélanger, J.M.R., Ng, S., Hawkins, R., 2010. Microwave applications to oil sand and petroleum: A review. Fuel Processing Technology 91, 127-135.
261. NanoRem 1., 2016. Nanotechnology for contaminated land remediation – possibilities and future trends resulting from the NanoRem project. CL: AIRE NanoRem bulletin.

262. National Academy of Science, 1975. Petroleum in the Marine shorelines of Prince William Sound Alaska. Environ. Sci. Environment, National Academy Press, Washington, D.C., Technol. 31 (5), 1564–1572.107.
263. Niazi., S., Hashemabadi, S.H., Razi, M.M., 2014. CFD simulation of acoustic cavitation in crude oil upgrading sonoreactor and prediction of collapse temperature and pressure of a cavitation bubble. Chemical Engineering Research and Design. 93(1), 166-173.
264. Nichols, E.G., Cook, R.L., Landmeyer, J.E., Atkinson, B., Malone, D.R., Shaw, G., Woods, L., 2014. Phytoremediation of a petroleum hydrocarbon contaminated shallow aquifer in Elizabeth City, North Carolina, USA. Remediation Spring, 29-46.
265. Njoku, K.L, Nomba, E.U., Olatunde, A.M., 2017. Vermiremediation of crude oil contaminated soil using *Eudrillus euginae* and *Lumbricus terrestris*. J. Biol. Environ. Sci. 11(13), 43-50.
266. Njoku, K.L., Yussuf, A., Akinola, M.O., Adesuyi, A.A., Jolaoso, A.O., Adedokun, A.H., 2016. Mycoremediation of petroleum hydrocarbon polluted soil by *Pleurotus pulmonarius*. Ethiopian Journal of Environmental Studies and Management 9(Suppl. 1), 865-875.
267. Nnaji, J.C., 2017. Anomaterials for remediation of petroleum contaminated soil and water. Umudike Journal of Engineering and Technology 3(2).
268. Nwankwegu, A.S., Onwosi, C.O., 2017. Bioremediation of gasoline contaminated agricultural soil by bioaugmentation. Environmental Technology & Innovation 7, 1-11.
269. Nyer, E.K., 2000. In situ treatment technology, second edition. Boca Raton, FL: CRC Press.
270. Nzila, A., Razzak, S.A., Zhu, J., 2016. Bioaugmentation: An emerging strategy of industrial wastewater treatment for reuse and discharge. International Journal of Environmental Research and Public Health 13,846.
271. O'Brien, P.L., DeSuther, T.M., Casey, F.X.M., Wick, A.F., Khan, E., 2017. Evaluation of soil function following remediation of petroleum hydrocarbons – a review of current remediation techniques. Curr Pollution Rep 3, 192.
272. O'Brien, P.L., DeSutter, T.M., Casey, F.X.M., Wick, A.F., Khan, E., 2017. Evaluation of soil function following remediation of petroleum hydrocarbons – a review of current remediation techniques. Curr Pollution Rep, 3(3), 192-205.
273. Ogunneye, A.L, Omoboyowa, D.A., Sonibare, A.L., Adebusuyi, A.J., Faniran, T.P., 2014. Hepatotoxicity and nephrotoxic effects of petroleum fumes on petrol attendants in Ibadan, Nigeria. Nigeria Journal of Basic and Applied Science, 22(3&8), 57-62.
274. Oil tanker spill statistics, 2016. The International Tanker Owners Pollution Federation Limited (1TOPF).
275. Okiel, K., El-Sayed, M., El-Kady, M.Y., 2011. Treatment of oil-water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. Egyptian Petroleum Research Institute. 20, 9-15.
276. Omoti, A.E., Waziri-Erameh, J.M., Enock, M.E., 2008. Ocular disorders in a petroleum industry in Nigeria. Eye 22, 925-929.
277. Ossai, I.C., Fauziah, S.H., Ghufran, R., 2014. The utilization of water hyacinth (*Eichhornia crassipes)* as an aquatic macrophage treatment system (AMATS) in phytoremediation for palm oil mill effluent (POME). International Journal of Sciences: Basic and Applied Research 13(2), 31-47.

278. Otto, M., Floyd, M., Bajpai, S., 2008. Nanotechnology for site remediation. Remediation 19(1), 99–108.
279. Ozen, A.S., Aviyente, V., Tezcanli-Guyer, G., Ince, N.H., 2005. Experimental and modeling approach to decolorization of azo dyes by ultrasound: degradation of the hydrazone tautomer. Journal of Physical Chemistry A 109 (15), 3506-3516.
280. Padmavathiamma, P.K., Li, L.Y., 2007. Phytoremediation technology: hyper-accumulation metals in plants. Water Air Soil Pollut. 184, 105-126.
281. Palma, E., Daghio, M., Franzetti, A., Papini, M.P., Aulenta, F., 2017. The bioelectric well: a novel approach for *in situ* treatment of hydrocarbon-contaminated groundwater. Microbial Biotechnology.
282. Pape, A., Switzer, C., McCosh, N., Knapp, C.W., 2015. Impacts of thermal and smouldering remediation on plant growth and soil ecology. Geoderma 243−244, 1–9.
283. Paterson, S., Mackay, D., Tam, D., Shiu, W.Y., 1990. Uptake of organic chemicals by plants: a review of processes, correlations and models. Chemosphere 21, 297-331.
284. Pearlman, L., 1999. Subsurface containment and monitoring systems: Barriers and beyond (Overview Report). National Network of Environmental Management Studies Fellow for U.S. Environmental Protection Agency.
285. Peixoto, R.S., Vermelho, A.S. and Rosado, A.S., 2011. Petroleum degrading enzymes: bioremediation and new prospects, Enzyme Research 7,
286. Pekdemir, T., Copur, M., Urum, K., 2005. Emulsification of crude oil—water systems using biosurfactants. Process Safety and Environmental Protection 83(B1), 38–46.
287. Peter, A.O., 2011. Enhanced bioremediation of soil contaminated with used lubricating oil. Doctoral Thesis, Institute of Biological Sciences, University of Malaya.
288. Peters, D.G., McGuire, C.M., Pasciak, E.M., Peverly, A.A., Strawsine, L.M., Wagoner, E.R., Barnes, J.T., 2014. Electrochemical dehalogenation of organic pollutants. J. Mex. Chem. Soc. 58(3), 287-302.
289. Pflieger, R., Chave, T., Virot, M., Nikitenko, S.I., 2014. Activating molecules, ions and solid particles with acoustic cavitation. J Vis Exp. 86, 51237.
290. Pham, T.D., 2014. Ultrasonic and electrokinetic remediation of low permeability soil contaminated with persistent organic pollutants. PhD Thesis, Lappenranta University of Technology. Finland.
291. Pham, T.D., Shrestha, R.A., Virkutyte, J., Sillanpaa, M., 2009. Combined ultrasonication and electrokinetic remediation for persistent organic removal contaminated kaolin. Electrochimica Acta 54, 1403-1407.
292. Phang, S.M., Chu, W.L., Rabiei, R., 2015. Phycoremediation. In: Sahoo D., Seckbach J. (eds) The Algae World. Cellular Origin, Life in Extreme Habitats and Astrobiology, vol 26. Springer, Dordrecht.
293. Philp, J.C., Atlas, R.M., 2005. Bioremediation of contaminated soils and aquifers. In: Atlas RM, Philp JC (eds) Bioremediation: applied microbial solutions for real-world environmental cleanup. American Society for Microbiology (ASM) Press, Washington, 139–236.
294. Pilon-Smits, E., 2005. Phytoremediation. Annual Review of Plant Biology 56, 15-39
295. Pironi, P., Switzer, C., Gerhard, J.I., Rein, G., Torero, J.L., 2011. Self-sustaining smoldering combustion for NAPL remediation: laboratory evaluation of process sensitivity to key parameters. Environ Sci Technol 45(7), 2980–2986.

296. Poi, G., Aburto-Medina, A., Mok, P.C., Ball, A.S., Shahsavari, E., 2017. Large-scale bioaugmentation of soil contaminated with petroleum hydrocarbons using a mixed microbial consortium. Ecological Engineering 102, 64-71.
297. Porch, A., Slocombe, D., Beutler, J., Edwards, P., Aldawsari, A., Xiao, T., Kuznetsov, V., Almegren, H., Aldrees, S., Almaqati, N., 2012. Microwave treatment in oil refining. Appl Petrochem Res 2, 37-44.
298. Potin, O., Rafin, C., Veignie, E., 2004. Bioremediation of an aged polycyclic aromatic hydrocarbons (PAHs)-contaminated soil by filamentous fungi isolated from the soil. Int. Biodeterior. Biodegrad. 54, 45–52.
299. Potter, T.L., and Simmons, K.E., 1998, Composition of petroleum mixtures: Amherst, Mass., Amherst Scientific Publishers, Total petroleum hydrocarbon criteria working group series 2, 102.
300. Prakash, V., Saxena, S., Sharma, A., Singh, S., Singh, S.K., 2015. Treatment of oil sludge contamination by composting. Journal of Bioremediation and Biodegradation 6(3), 284.
301. Price, S.L., Kasevich, R.S., Johnson, M.A., Wilberg, D., Marley, M.C., 1999. Radio frequency heating for soil remediation. Journal of the Air and Waste Managmenet Association 49(2), 136-145.
302. Pueh, LLL., 2010. In-situ photocatalytic remediation of organic contaminants in groundwater. Doctoral Dissertation, University of Cambridge, United Kingdom.
303. Rahsepar, S., Smit, M.P.J., Murk, A.J., Rijnaarts, H.H.M., Langenhoff, A.A.M., 2016. Chemical dispersants: oil biodegradation friends or foe? Marine Pollution Bulletin.
304. Rajamanickam, D., Shanthi, M., 2016. Photocatalytic degradation of an organic pollutant by zinc oxide – solar process. Arabian Journal of Chemistry 9, S1858-S1868.
305. Razzaq, R., 2017. Phytoremediation: an environmental friendly technique – a review. Journal of Environmental Analytical Chemistry 4(2), 195
306. Reddy, K.R., 2013. Electrokinetic remediation of soils at complex contaminated sites: Technology status, challenges, and opportunities. In Coupled Phenomena in Environmental Geotechnics. Francis & Taylor group. 131 - 147.
307. Reddy, K.R., Darko-Kagya, K., Cameselle, C., 2011. Electrokinetics-enhanced transport of lactate modified nanoscale iron particles for degradation of dinitrotoluene in clayey soils. Separation and Purification Technology 79, 230-237.
308. Reddy, K.R., Maturi, K., Cameselle, C., 2009. Sequential electrokinetic remediation of mixed contaminants in low permeability soils. Journal of Environmental Engineering 135(10)
309. Ren, X., Zeng, G., Tang, L., Wang, J., Wang, J., Deng, Y., Liu, Y., Peng, B., 2018. The potential impact on the biodegradation of organic pollutants from composting technology for soil remediation. Waste Management 72, 138-149.
310. Riazi, M.R., 2005. Characterization and properties of petroleum fractions. (1st ed.) American Society for Testing and Material (ASTM), West Conshohocken, PA.
311. Riser-Roberts, E., 1998. Remediation of petroleum contaminated soils. Biological, physical and chemical processes. Lewis Publishers, United States of America.
312. Robertson, D., Burnley, S., Barratt, R., 2003. The Immobilization of flue gas treatment residues through the use of a single staged wash and crystalline matrix encapsulation (CME) treatment process, Proceedings of the 11th Annual North American Waste to Energy Conferences (NAWTEC11), Apr 28–30 2003, Tampa, FL, pp. 135–143.

313. Robinson, J.P., Kingman, S.W., Snape, C.E., Barranco, R., Shang, H., Bradley, M.S.A., Bradshaw, S.M., 2009. Remediation of oil-contaminated drill cuttings using continuous microwave heating. Chemical Engineering Journal 152, 458-463.
314. Rock, S., Pivetz, B., Madalinski, K., Adams, N., Wilson, T., 2000. Introduction to phytoremediation. U.S. Environmental Protection Agency, Washington DC., EPA/600/R-99/107 (NTIS PB2000-106690)
315. Rodrigo, M.A., Oturan, N., Oturan, M.A., 2014. Electrochemically assisted remediation of pesticides in soil and water: A review. Chem. Rev., 114(17), 8720-8745.
316. Rodriguez-Freire, L., Abad-Fernández, N., Sierra-Alvarez, R., Hoppe-Jones, C., Peng, H., Giesy, J.P., Snyder, S., Keswani, M., 2016. Sonochemical degradation of perfluorinated chemicals in aqueous film-forming foams. Journal of Hazardous Materials. 317, 275-283.
317. Rodriques, E.M., Totola, M.R. 2015. Petroleum: from basic features to hydrocarbons bioremediation in oceans. Open Access Library Journal, vol 2.
318. Ron, E.Z., and Rosenberg, E., 2014. Enhanced bioremediation of oil spills in the sea. Curr. Opin. Biotechnol. 27, 191-194.
319. Roser, M. 2017. Oil Spills. Published online at OurWorldInData.org. Retrieved from: 'https://ourworldindata.org/oil-spills' [Online Resource] 29 January2017.
320. Rumer, R. R., Ryan, M.E., 1995. Barrier containment technologies for environmental remediation applications. New York, Wiley.
321. Rusin, M., Gospodarek, J. and Nadgórska-Socha, A., 2015. The Effect of Petroleum-Derived Substances on the Growth and Chemical Composition of *Vicia faba* L. Pol. J. Environ. Stud. 24(5), 2157-2166.
322. Saichek, R., Reddy, K., 2005. Electrokinetically enhanced remediation of hydrophobic organic compounds in soils: A review. Critical Reviews in Environmental Science and Technology 35, 115–192.
323. Sajna, K.V., Sukumaran, R.K., Gottumukkala, L.D., Pandey, A., 2015. Crude oil biodegradation aided by bio-surfactants from *Pseudozyma sp*. NII 08165 or its culture broth. Bioresour. Technol. 191, 133–139.
324. Saksa, P., 2017. Electrically assisted soil remediation. INSURE Geosto Report.
325. Sammarco, P.W., Kolian, S.R., Warby, R.A.F., Bouldin, J.L., Subra, W.A., Porter, S.A., 2016. Concentrations in human blood of petroleum hydrocarbons associated with the BP/Deepwater Horizon oil spill, Gulf of Mexico. Arch. Toxicol. 90, 829–837.
326. Sankula, K., Kota, S., Nissankarrao, S., 2014. Supercritical fluid technology: green chemistry for the 21st century. The Pharma Innovation Journal 3(5), 19-24.
327. Sapkale, G.N., Patil, S.M., Surwase, U.S., Bhatbhage, P.K., 2010. Supercritical fluid extraction. A review. Int. J. Chem. Sci. 8(2), 729-743.
328. Saravanam, R., Gracia, F., Stephen, A., 2017. Basic principles, mechanisms, and challenges of photocatalysis. In: Khan, M.M., Pradhan, D., Sohn, Y., (Eds). Nanocomposites for visible light induced. Springer.
329. Saum, L., Jiménez, M.B., Crowley, D., 2018. Influence of biochar and compost on phytoremediation of oil-contaminated soil. Int. J. Phytoremediation 20(1), 54-60.
330. Schaefer, M., Juliane, F., 2007. The influence of earthworms and organic additives on the biodegradation of oil contaminated soil. Appl. Soil Ecol. 36(1), 53-62.

331. Schnoor, J. L., Licht, L. A., McCutcheon, S. C., Wolfe, N. L., Carreira, L. H., 1995. Phytoremediation of organic and nutrient contaminants. Environ. Sci. Technol. 29, 318-323.
332. Scholes, G.C., Gerhard, J.I., Grant, G.P., Major, D.W., Vidumsky, J.E., Switzer, C., et al., 2015. Smoldering remediation of coal-tar-contaminated soil: pilot field tests of STAR. Environ Sci Technol. 49(24), 14334–42.
333. Sempel, K.T., Morris, A.W.J. and Paton, G.I., 2003. Bioavalaibility of hydrophobic organic contaminants in soils; fundamental concepts and techniques for analysis. European Journal of Soil Science 54, 809-818.
334. Seo, S.J., Kim, J.H., Shin, J.W., Park, J.Y., 2015. Treatment of artificial and real co-contaminated soil by an enhanced electrokinetic-fenton process with a soil flushing method. Water Air & Soil Pollution 226, 86.
335. Shan, B.Q, Zhang, Y.T, Cao, Q.L., 2014. Growth responses of six leguminous plants adaptable in Northern Shaanxi to petroleum-contaminated soil. Environmental Science 35, 1125-1130.
336. Sharma, S., 2012. Bioremediation: features, strategies and applications. Asian Journal of Pharmacy and Life Science 2(2), 202-213.
337. Sheppard, S. C., Evenden, W.G., 1985. Mobility and uptake by plants of elements placed near a shallow water table interface. J. Environ. Qual. 14, 554- 560.
338. Shrestha, R.A., Mudhoo, A., Pham T-D., Sillapaa, M., 2011. Ultrasound and sonochemistry in the treatment of contaminated soils by persistent organic pollutants. In: Chen, D., Sharma, S.K., Mudhoo, A., (Eds.). Handbook of application of ultrasounds: sonochemistry and sustainability. CRC Press
339. Silva, A., Delerue-Matos, C., Fiuza, A., 2005. Use of solvent extraction to remediate soils contaminated with hydrocarbons. Journal of Hazardous Materials B124, 224-229.
340. Simpanen, S., 2016. Evaluation of in-situ remediation methods in soils contaminated with organic pollutants. Dissertation in Environmental Ecology, University of Helsinki, Lahti, Finland.
341. Simpanen, S., Dahl, M., Gerlach, M., Mikkonen, A., Malk, V., Mikola, J., Romantschuk, M., 2016. Biostimulation proved to be the most efficient method in the comparison of in situ soil remediation treatments after a simulated oil spill accident. Environ Sci Pollut Res. 23, 25024-25038.
342. Sims, J.L., Suflita, J.M., Russell, H.H., 1991. Reductive dehalogenation of organic contaminants in soil and ground water. EPA Ground Water Issue. EPA/540/4-90/054.
343. Singh, B., Bhattacharya, A., Channashettar, V.A., Jeyaseelan, C.P., Gupta, S., Sarma, P.M., Mandal, A.K., Lal, B., 2012. Biodegradation of oil spill by petroleum refineries using consortia of novel bacterial strains. Bull. Environ. Contam. Toxicol. 89, 257-262.
344. Singh, S., 2012. Phytoremediation: a sustainable alternative for environmental challenges. Int J Gr Herb Chem 1, 133-139.
345. Singh, S.N., Kumari, B., Mishra, S., 2012. Microbial degradation of alkanes. In: Singh, S.N (ed.), Microbial degradation of xenobiotics. Environmental Science and Engineering, Springer-Verlag Berlin Heidelberg. DOI: 10.1007/978-3-642-23789-8_17.
346. Singh, S.P., Garima, T., 2015. Application of bioremediation on solid waste management: A review. Environmental Science An Indian Journal 10(1).
347. Sinha, R.K., Bharambe, G., Ryan, D., 2008. Converting wasteland into wonderland by earthworms—a low-cost nature's technology for soil remediation: a case study of

vermiremediation of PAHs contaminated soil. The Environmentalist: the Inter. J. for all Environmental Professionals, 28(4), 466-475.
348. Sivagami, K., Padmanabhan, K., Joy, A.C., Nambi, I.M., 2019. Microwave (MW) remediation of hydrocarbon contaminated soil using spent graphite – an approach for waste as a resource. Journal of Environmental Management 230, 151-158.
349. Smitha, M.S., Singh, S., Singh, R., 2017. Microbial biotransformation: a process for chemical alterations. Journal of Bacteriology and Mycology: Open Access 4(2)
350. Snape, I., Riddle, M.J., Stark, J.S., Cole, C.M., King, C.K., Duquesne, S., Gore, D.B., 2001. Management and remediation of contaminated sites at Casey Station, Antarctica. Polar Rec. 37, 199-214.
351. Song, X., 2011. Remediation of salt and petroleum hydrocarbon contaminated soil using ultrasound and soil washing. Dissertation, University of Northern British Columbia.
352. Song, Y.L., Li, J.T., 2009. Degradation of CI Direct Black 168 from aqueous solution by fly ash/H_2O_2 combining ultrasound. Ultrasonics Sonochemistry 16 (4), 440-444.
353. Soroush, F., Ganjidoust, H., Ayati, B., 2017. Removal of petroleum hydrocarbons from contaminated waters using a solar photocatalytic process. Journal of Ferdowsi Civil Engineering, 29(1).
354. Souza, E.C., Vessoni-Penna, T.C., de Souza Oliveira, R.P., 2014. Biosurfactant enhanced hydrocarbon bioremediation: an overview. Int. Biodeterior. Biodegrad. 89, 88-94.
355. Speight, J.G., 2001. Handbook of petroleum analysis, New York, John Wiley.
356. Speight, J.G., 2007. The Chemistry and Technology of Petroleum. CRC, Taylor and Francis, Boca Raton, Florida, U.S.A. Vol. 114.
357. Speight, J.G., 2014. The Chemistry and Technology of Petroleum, 5th ed. CRC press, Boca Raton, Florida, USA
358. Srikanth, S., Kumar, M., Puri, S.K, 2018. Bio-electrochemical system (BES) as an innovative approach for sustainable waste management in petroleum industry. Bioresour. Technol. https://doi.org/10.1016/j.biortech.2018.02.059.
359. Srikanth, S., Kumar, M., Singh, D., Singh, M.P., Das, B.P., 2016. Electro-biocatalytic treatment of petroleum refinery wastewater using microbial fuel cell (MFC) in continuous mode operation. Bioresour. Technol. 221, 70–77.
360. Srinivasan, A., Chowdhury, P., Viraraghan, T., 2008. Air stripping in industrial wastewater treatment. In book: ELOSS – Waste Water Treatment Technologies
361. Sriram K, Lin GX, Jefferson AM, Goldsmith WT, Jackson M, McKinney W, et al. Neurotoxicity following acute inhalation exposure to the oil dispersant COREXIT EC9500A. J. Toxicol Environ Health A 74:1405–18.
362. Stegemeier, G.L., Vinegar, H.J., 2001. Thermal conduction heating for in-situ thermal desorption of soils. In: Oh CH, editor Hazardous and radioactive waste treat-ment technologies handbook. Boca Raton: CRC Press
363. Størdal, I.F., Olsen, A.J., Jenssen, B.M., Netzer, R., Altin, D., Brakstad, O.B., 2015. Biotransformation of petroleum hydrocarbons and microbial communities in seawater with oil dispersions and copepod feces. Marine Pollution Bulletin 101, 686-693.
364. Stroud, J.L., Paton, G.I. and Sempel, K.T., 2009. Predicting the biodegradation of target hydrocarbons in the presence of mixed contaminants in soil. Chemosphere 74(4), 563-567.

365. Stroud, J.L., Paton, G.I., Semple, K.T., 2007. Microbe-aliphatic hydrocarbon interactions in soil: implications for biodegradation and bioremediation. J. Appl. Microbiol. 102, 1239-1253.
366. Subashchandrabose, S.R., Ramakrishnan, B., Megharaj, M., Venkateswarlu, K., Naidu, R.R., 2013. Mixotrophic cyanobacteria and microalgae as distinctive biological agents for organic pollutant degradation. Environ Int. 51, 59-72.
367. Suzuki, H., Yamagiwa, S., Araki, S., Yamamoto, H., 2016. Effects of advanced oxidation process on the decomposition properties of organic compounds with different molecular structures in water. Journal of Water Resources and Protection 8, 823-834.
368. Switzer, C, Pironi, P., Gerhard, J.I., Rein, G., Torero, J.L., 2009. Self-sustaining smoldering combustion: a novel remediation process for non-aqueous-phase liquids in porous media. Environ Sci Technol 43(15), 5871−5877.
369. Switzer, C., Pironi, P., Gerhard, J.I., Rein, G., Torero, J.L., 2014. Volumetric scale-up of smouldering remediation of contaminated materials. J Hazard Mater. 268, 51–60.
370. Tadros, T.E., 2013. Emulsion formation, stability and rheology. In: Tadros T.F., (Ed.). Emulsion formation and stability. Wiley-VCH Verlag GmbH & Co. KGaA.
371. Tang, W.Z., 2003. Physicochemical treatment of hazardous wastes. CRC Press, USA.
372. Techneau, 2010. Advanced oxidation process. Degradation of priority compounds by UV and UV-oxidation. KWR Watercycle Research Institute.
373. Thavamani, P., Smith, E., Kavitha, R., Mathieson, G., Megharaj, M., Srivasta, P., Naidu, R., 2015. Risk based land management requires focus beyond the target contaminants – a case study involving weathered hydrocarbon contaminated soils. Environmental Technology & Innovation 4, 98-109.
374. Theron, J., Walker, J.A., Cloete, T.E., 2008. Nanotechnology and water treatment: applications and emerging opportunities. Crit Rev Microbiol. 34, 43–69.
375. Thomé, A., Reddy, K.K., Reginatto, C., Cecchin, I., 2015. Review of nanotechnology for soil and groundwater remediation: Brazilian perspectives. Water, Air, Soil Pollut. 226, 1-20.
376. Thomé, A., Reginatto, C., Cecchin, I., Colla, L.M., 2014. Bioventing in a residual clayey soil contaminated with a blend of biodiesel and diesel oil. J. Environ. Eng. 140.
377. Toth, A.J., Mizsey, P., 2015. Comparison of air and steam stripping: removal of organic halogen compounds from process wastewaters. Int. J. Environ Sci. Technol. 12:1321-1330.
378. Trach, R.J. 1996. Ultraviolet/oxidation treatment. Technical Overview Report. Ground Water Remediation Technology Analysis Center. TO-96-06
379. Transportation Research Board and National Research Council. 2003. Oil in the Sea III: Inputs, Fates, and Effects. Washington, DC: The National Academies Press. https://doi.org/10.17226/10388.
380. Trulli, E., Morosini, C., Rada, E.C., Torretta, V., 2016. Remediation in situ of hydrocarbons by combined treatment in a contaminated alluvial soil due to an accidental spill of LNAPL. Sustainability 8, 1086.
381. Tuhuloula, A., Altway, A., Juliastuti, S.R., Suprapto, S., 2014. Biodegradation of soils contaminated with naphthalene in petroleum hydrocarbons using bioslurry reactors. IOP Conf Series: Earth and Environmental Science 175, 012014

382. Tyagi, M., da Fonseca, M. M. R., and de Carvalho, C., 2011. Bioaugmentation and biostimulation strategies to improve the effectiveness of bioremediation processes. Biodegradation 22, 231–241.
383. Umar, A.A., Saaid, I.B.M., Sulaimon, A.A., Pilus, R.B.M., 2018. A review of petroleum emulsions and recent progress on water-in-crude oil emulsions stabilized by natural surfactants and solids. Journal of Petroleum Science and Engineering 165, 673-690.
384. Umar, M., Abdul Aziz, H., 2013. Photocatalytic degradation of organic pollutants in water. Organic Pollutants In: Rasheed, M.N., (Ed). Monitoring, Risk and Treatment, InTech 8, 195-208.
385. United States Environmental Protection Agency (USEPA), 1986. Test method for evaluating solid waste, SW-846, 3rd Ed., Vol. 1A. U.S. EPA, Washington, DC.
386. United States Environmental Protection Agency (USEPA), 1997. Engineering bulletin: Technology alternatives for the remediation of soils contaminated with As, Cd, Cr, Hg, and Pb, EPA/540/S -97/500. Washington DC: Office of Emergency and Remedial Responses; Cincinnati, OH: Office of Research and Development.
387. United States Environmental Protection Agency (USEPA), 1997. Innovative site remediation design and application, Stabilization/Solidification, EPA 542/B-97/007. Office of Solid Waste and Emergency Response, 4
388. United States Environmental Protection Agency (USEPA), 2006. In situ treatment technologies for contaminated soil. Engineering Forum Issue Paper. Solid Wates and Emergency Response 5203P. EPA 542/F-06/013.
389. United States Environmental Protection Agency (USEPA), 2007. Technology reference guide for radioactively contaminated media. Office of Radiation and Indoor Air Radiation Protection Programme. EPA 402-R-07-004.
390. United States Environmental Protection Agency (USEPA), 2012. Green remediation best management practices: Implementing in situ thermal technologies. Office of Solid Waste and Emergency Response, EPA 542-F-12-029.
391. United States Environmental Protection Agency (USEPA), 2018. Remedial technology fact sheet – activated carbon – based technology for in situ remediation. EPA 542-F-18-001
392. United States Environmental Protection Agency (USEPA), 2000. Introduction to phytoremediation. EPA 600/R-99/107, U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH.
393. United States Environmental Protection Agency (USEPA), 2001. A Citizen's Guide to Solvent Extraction. US Environmental Protection Agency, Washington, DC
394. United States National Academy of Sciences, 2002. Oil in the sea III: Inputs, fates and effects. Report by the National Research Council (NRC) Committee on Oil in the Sea: Inputs, Fates, and Effects.
395. Vajnhandl, S., Le Marechal, A.M., 2007. Case study of the sonochemical decolouration of textile azo dye Reactive Black 5. Journal of Hazardous Materials 141 (1), 329-335.
396. Vajnhandl, S., Marechal, A.M.L., 2005. Ultrasound in textile dyeing and the decolourization/mineralization of textile dyes. Dyes Pigments 65, 89–101.
397. Valentin, L., Nousiainen, A., Mikkonen, A., 2013. Emerging organic contaminants in sludges: analysis, fate and biological treatment. Hdb. Env. Chem. 24, 1-30.
398. Van der Heul R. M., 2009. Environmental degradation of petroleum hydrocarbons. Utrecht

University.http://studenttheses.library.uu.nl/search.php?language=en&qry=Environmental+Degradation+of+petroleum+hydrocarbons. (Accessed Jan 2018)

399. Van Hamme, J. D., Singh, A., Ward, O. P., 2003. Recent advances in petroleum microbiology. Microbiol. Mol. Biol. Rev. 67, 503–549.
400. Varjani, S.J. 2017. Microbial degradation of petroleum hydrocarbons. Bioresource Technology 223, 277-286.
401. Varjani, S.J., Rana, D.P., Jain, A.K., Bateja, S., Upasani, V.N., 2015. Synergistic ex situ biodegradation of crude oil by halotolerant bacterial consortium of indigenous strains isolated from on shore sites of Gujarat, India. Int. Biodeterior. Biodegrad. 103, 116-124.
402. . Varjani, S.J., Upasani, V.N., 2017. A new look on factor affecting microbial degradation of petroleum hydrocarbon pollutants. International Biodeterioration & Biodegradation 120:71-83
403. Vasilyeva, G.K., Strijakova, E.R., Shea, P.J., 2006. Use of activated carbon for soil bioremediation. In: Twardowska, I., Allen, H.E., Haggbrom, M.H., (eds). Soil and Water Pollution Monitoring, Protection and Remediation, 3-23.
404. Vásquez-Murrieta, M.S., Hernández-Hernández, O.J., Cruz-Maya, J.A., Cancino-Díaz, J.C. and Jan-Roblero, J., 2016. Approaches for Removal of PAHs in Soils: Bioaugmentation, Biostimulation and Bioattenuation. INTECH. Environmental Sciences. Soil Contamination - Current Consequences and Further Solutions.
405. Vavrek, M. C., Campbell, W. J., 2002. Contribution of seed banks to freshwater wetland vegetation recovery. Louisiana Applied and Educational Oil Spill Research and Development Program, OSRADP. Technical Report Series, 0-12.
406. Veenis, Y.M.M., Heling, R.K., 2014. Field demonstration project steam enhanced remediation Greenwich Mohawk site, city of Brantford, Ontario, Canada. Groundwater Technology BV.
407. Venderbosch, R., Ardiyanti, A., Wildschut, J., Oasmaa, A., Heeres, H., 2010. Stabilization of biomass derived pyrolysis oils. J Chem Technol Biotechnol 85, 674–686.
408. Ventikos, N.P., Vergetis, E.O., Psaraftis, H.N., Triantafyllou, G., 2004. A high-level synthesis of oil spill response equipment and countermeasure. Journal of Hazardous Materials 107(1-2), 51-58.
409. Vidonish, J.E, Zygourakis, K., Masiello, C.A., Gao, X., Mathieu, J., Alvarez, P.J., 2016a. Pyrolytic treatment and fertility enhancement of soils contaminated with heavy hydrocarbons. Environ Sci Technol 50(5), 2498–506.
410. Vidonish, J.E., Zygourakis, K., Masiello, C.A., Sabadell, G., Alvarez, P.J.J., 2016b. Thermal treatment of hydrocarbon-impacted soils: A review of technology innovation for sustainable remediation. Engineering 2, 426-437.
411. Virkutyte, J., Sillanpaa, M., Latostenmaa, P., 2002. Electrokinetic soil remediation – critical overview. Sci Total Environ. 289, 97-121.
412. Vu, T.H., Tran, M.V., 2018. A review on immobilisation of toxic wastes using geopolymer technique. In: Tran-Nguyen H.H., Wong, H., Ragueneau, F., Ha-Minh C. (eds) Proceedings of the 4th Congrès International de Géotechnique - Ouvrages - Structures. CIGOS 2017. Lecture Notes in Civil Engineering, vol 8. Springer, Singapore.
413. Wagner, A.M., Yarmak Jr., E., 2017. Using frozen barriers for containment of contaminants. Installation Technology Transfer Programme. ERDC/CRREL TR-17-14.

414. Wami, Emenike, Nyeche, Nmegbu, Chukwuma, G.J., 2015. Micro-encapsulation technique for effective remediation of hydrocarbon contaminants. International Journal of Scientific and Engineering Research 6(8), 315-323.
415. Wang, H., Luo, H., Fallgren, P.H., Jin, S., Ren, Z.J., 2015. Bioelectrochemical system platform for sustainable environmental remediation and energy generation. Biotechnol. Adv. 33(3-4), 317-334
416. Wang, S.Y., Kuo, Y.C., Hong, A., Chang, Y.M., Kao, C.M., 2016. Bioremediation of diesel and lubricant oil contaminated soil using enhanced landfarming system. Chemosphere 164, 558-567.
417. Wang, Z.Y., Xu, Y., Zhao, J., Li, F.M., Gao, D.M., Xing, B.S., 2011. Remediation of petroleum contaminated soils through composting and rhizosphere degradation. J. Hazard. Mater. 190, 677–685.
418. Whelan, M.J., Coulon, F., Hince, G., Rayner, J., McWatters, R., Spedding, T., Snape, I., 2015. Fate and transport of petroleum hydrocarbons in engineered biopiles in Polar Regions. Chemosphere 131, 232–240.
419. Williams, S.D., Ladd, D.E., and Farmer, J.J., 2006, Fate and transport of petroleum hydrocarbons in soil and ground water at Big South Fork National River and Recreation Area, Tennessee and Kentucky, 2002-2003: U.S. Geological Survey Scientific Investigations Report 2005-5104, p 29.
420. Wongsa, P., Tanaka, M., Ueno, A., Hasanuzzaman, M., Yumoto, I., Okuyama, H., 2004. Isolation and characterization of novel strains of *Pseudomonas aeruginosa* and *Serratia marcescens* possessing high efficiency to degrade gasoline, kerosene, diesel oil, and lubricating oil. Curr. Microbiol. 49, 415–422.
421. World Health Organization [WHO] (1986) In, Immunotoxicology: Development of predictive testing for determining the immunotoxic potential of chemicals. United Nations Environment Programme International Labor Office, Report of a Technical Review Meeting, WHO Press, London, U.K.
422. Wu, G., and Coulon, F., 2015. Protocol for Biopile Construction Treating Contaminated Soils with Petroleum Hydrocarbons. In: McGenity T., Timmis K., Nogales B. (eds) Hydrocarbon and Lipid Microbiology Protocols. Springer Protocols Handbooks. Springer, Berlin, Heidelberg.
423. Wu, G., Coulon, F., Yang, Y., Li, H., Sui, H., 2013. Combining solvent extraction and bioremediation for removal of weathered petroleum in soil. Pedosphere 23(4), 455-463.
424. Wu, M., Dick, W.A., Li, W., Wang, X., Yang, Q., Wang, T., Xu, L., Zhang, M., Chen, L., 2016. Bioaugmentation and biostimulation of hydrocarbon degradation and the microbial community in a petroleum contaminated soil. International Biodeterioration and Biodegradation 107, 158-164.
425. Wu, M., Li, W., Dick, W.A., Ye, X., Chen, K., Kost, D., Chen, L., 2017. Bioremediation of hydrocarbon degradation in a petroleum contaminated soil and microbial population and activity determination. Chemosphere 169, 124-130.
426. Wu, T.Y., Guo, N., Teh, C.Y., Hay, J.X.W., 2013. Advances in ultrasound technology for environmental remediation. SpringerBriefs in Green Chemistry for Sustainability. DOI: 10.1007/978-94-007-5533-8_2.
427. Wulandari, M., Effendi, A.J., 2014. Effect of frequency and ratio solid liquid on ultrasonic remediation of petroleum contaminated soil. International Conference on Science and Applied Science (ICSAS), AIP Conf. Proc. 020120-1–020120-7

428. Xu, Y., Zhang, C., Zhao, M., Rong, H., Zhang, K., Chen, Q., 2016. Comparison of bioloeaching and electrokinetic remediation processes for removal of heavy metals from wastewater treatment sludge. Chemosphere 168, 1152-1157.
429. Yadav, K.K., Singh, J.K., Gupta, N., Kumar., V., 2017. A review of nanobioremediation technologies for environmental cleanups: A novel biological approach. Journal of Materials and Environmental Sciences. 8(2), 740-757.
430. Yamada-Onodera, K., H. Mukumoto, Y. Katsuyaya 2001. Degradation of polyethylene by a fungus, *Penicillium simplicissimum* YK. Polym. Degrad. Stab. 72, 323–327.
431. Yang, C., Kublik, A., Weidauer, C., Seiwert, B., Adrian, L., 2015. Reductive dehalogenation of oligocyclic phenolic bromoaromatics by Dehalococcoides mccartyi Strain CBDB1. Environmental Science & Technology 49 (14), 8497-8505.
432. Yang, Y., Javed, H., Zhang, D., Li, D., Kamath, R., McVey, K., Sra, K., Alvarez, P.J.J., 2017. Merits and limitation of TiO2 based photocatalytic pretreatment of soils impacted by crude oil for expediting bioremediation. Frontiers of Chemical Science and Engineering 11(3), 387-394.
433. Yanti, M.D. 2018. Bioremediation of petroleum contaminated soil: A review. IOP Conference Series: Earth Environ. Sci. 118.
434. Yeung, A.T., 2010. Remediation technologies for contaminated sites. In: Chen, Y., Zhan, L., Tang, X., (eds). Advances in environmental geotechnics. Hangzhou: Zhejiang University Press, 328–69.
435. Yu, Li., Han, M., He, F., 2017. A review of treating oily wastewater. Arabian Journal of Chemistry 10, S1913-S1922
436. Zamani, M.M., Fallahpour, M., Harvani, G.Y., Aghmiuni, S.K., Mamani, M., Tehrani, D.M., Firrozabadi, G.S., 2014. Recent proportionate treatment methods for crude oil contamination evaluation of the Tehran refinery site soil. THRITA 3(1) 12113.
437. Zanaroli, G., Negroni, A., Haggblom, M.M., Fava, F., 2015. Microbial dehalogenation of organohalides in marine and estuarine environments. Current Opinion in Biotechnology 33, 287-295.
438. Zappi, M.E., Bajpai, R., Hernandez, R., Taconi, K. and Gang, D., 2017. Reclamation of smaller volumes of petroleum hydrocarbon contaminated soil using an innovative reactor system: A case study evaluation of the design. Agricultural Sciences, 8, 600-615.
439. Zhang, C., Chen, X., Tan, Y., Feng, Y., Zhong, Z., 2015. Soil vapour extraction removal of semi volatile organic compounds in soil: A pilot-scale study. International Conference on Sustainable Energy and Environmental Engineering. 180-182.
440. Zhang, T., Tremblay, P.L., Chaurasia, A.K., Smith, J.A., Bain, T.S., and Lovley, D.R., 2013. Anaerobic benzene oxidation via phenol in *Geobacter metallireducens*. Appl Environ Microbiol 79: 7800–7806.
441. Zhang, W.X., 2003. Nanoscale iron particles for environmental remediation: an overview. J Nanopart Res. 5, 323–332.
442. Zhao, C., Dong, Y., Feng, Y., Li, Y., Dong, Y., 2019. Thermal desorption for remediation of contaminated soil: A review. Chemosphere 221, 841-855
443. Zheng, M., Ahuja, M., Bhattacharya, D., Clement, T.P., Hayworth, J.S., Dhanasekaran, M., 2014. Evaluation of differential cytotoxic effects of the oil spill dispersant Corexit 9500. Life Science. 95, 108-117.
444. Zhu, W., 2010. Petroleum polluted soil and sludge bio-treatment technology. Beijing: China petrochemical press. 26-29.

445. Zhu, X., Venosa, A.D., Suidan, M.T., 2001. Guidelines for the bioremediation of marine shoreline and freshwater wetlands. Cincinnati, OH: USEPA.
446. Zolfaghari-Baghbaderani, A., Emtyazjoo, M., Poursafa, P., Mehrabian, S., Bijani, S., Farkhani, D., Mirmoghtadaee, P., 2012. Effects of three types of oil dispersants on biodegradation of dispersed crude oil in water surrounding two Persian Gulf provinces. Journal of Environmental and Public Health.

Journal Pre-proof

Journal Pre-proof

Table 1. **Petroleum hydrocarbon classes and characteristics**

Hydrocarbons	Characteristics	Examples
Aliphatics • Alkanes • Alkenes • Alkynes	• Less dense than water • Molecule size is inversely proportional to its volatility and water solubility	Methane, propane, butane (gas at room temperature); hexane, octane hexadecane (liquid at room temperature); eicosane, triacontane, pentacontane (solid at room temperature
Cycloaliphatics • Cycloalkanes	• Contains up to six carbon atoms in a ring • Fairly resistant to microbial degradation	Cyclohexane, methyl cyclohexane, methylcyclopentane, 1,2-dimethylcyclopentane
Aromatics • Monoaromatics BTEX • PAH	• Very volatile and relatively water-soluble • Have benzene ring • Some are resistant to microbial degradation	Benzene, ethylbenzene, naphthalene, toluene, xylene and phenanthrene
Other components • Asphaltenes • Waxes and tar • Resins • Non-hydrocarbon compounds	• Soluble in aromatics and non-soluble in light alkanes • Contains about 18 to 65 carbon atoms	Phenols, fatty acids, ketones, esters, porphyrins, pyridines, quinolines, cardaxoles, sulphonates

Journal Pre-proof

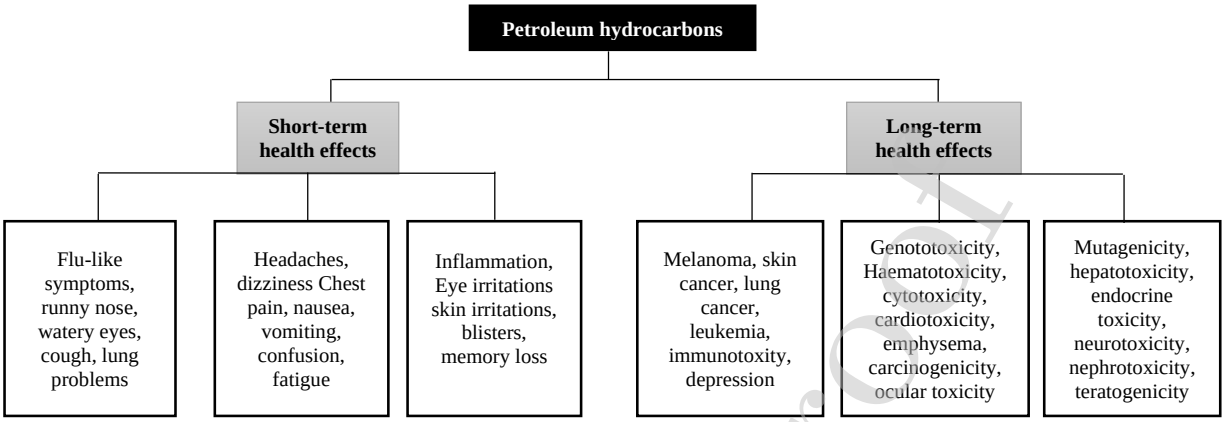

Petroleum hydrocarbons
Short-term health effects
Long-term health effects
Flu-like symptoms, runny nose, watery eyes, cough, lung problems
Headaches, dizziness Chest pain, nausea, vomiting, confusion, fatigue
Inflammation, Eye irritations skin irritations, blisters, memory loss
Melanoma, skin cancer, lung cancer, leukemia, immunotoxity, depression
Genototoxicity, Haematotoxicity, cytotoxicity, cardiotoxicity, emphysema, carcinogenicity, ocular toxicity
Mutagenicity, hepatotoxicity, endocrine toxicity, neurotoxicity, nephrotoxicity, teratogenicity

Figure 1 **Toxicological health effects of overexposure to petroleum hydrocarbons**

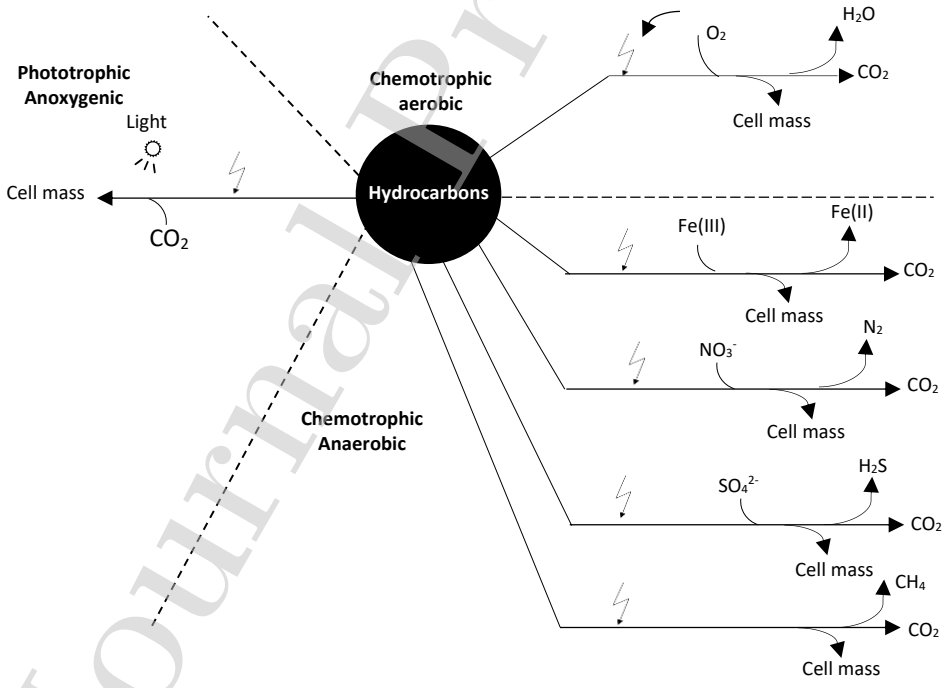


Figure 2 **Degradation mechanisms for petroleum hydrocarbons**

Journal Pre-proof

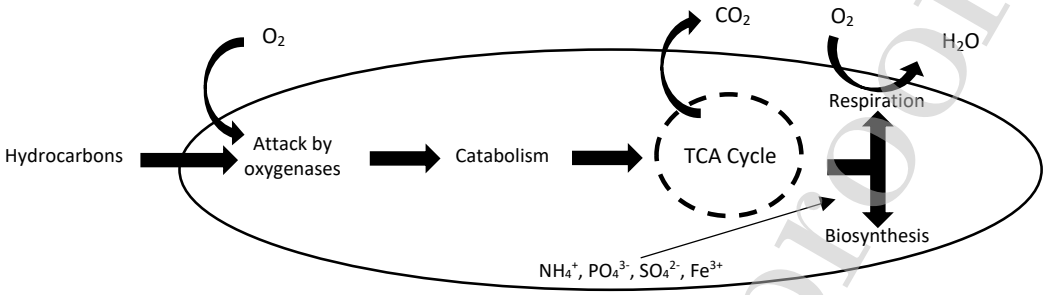
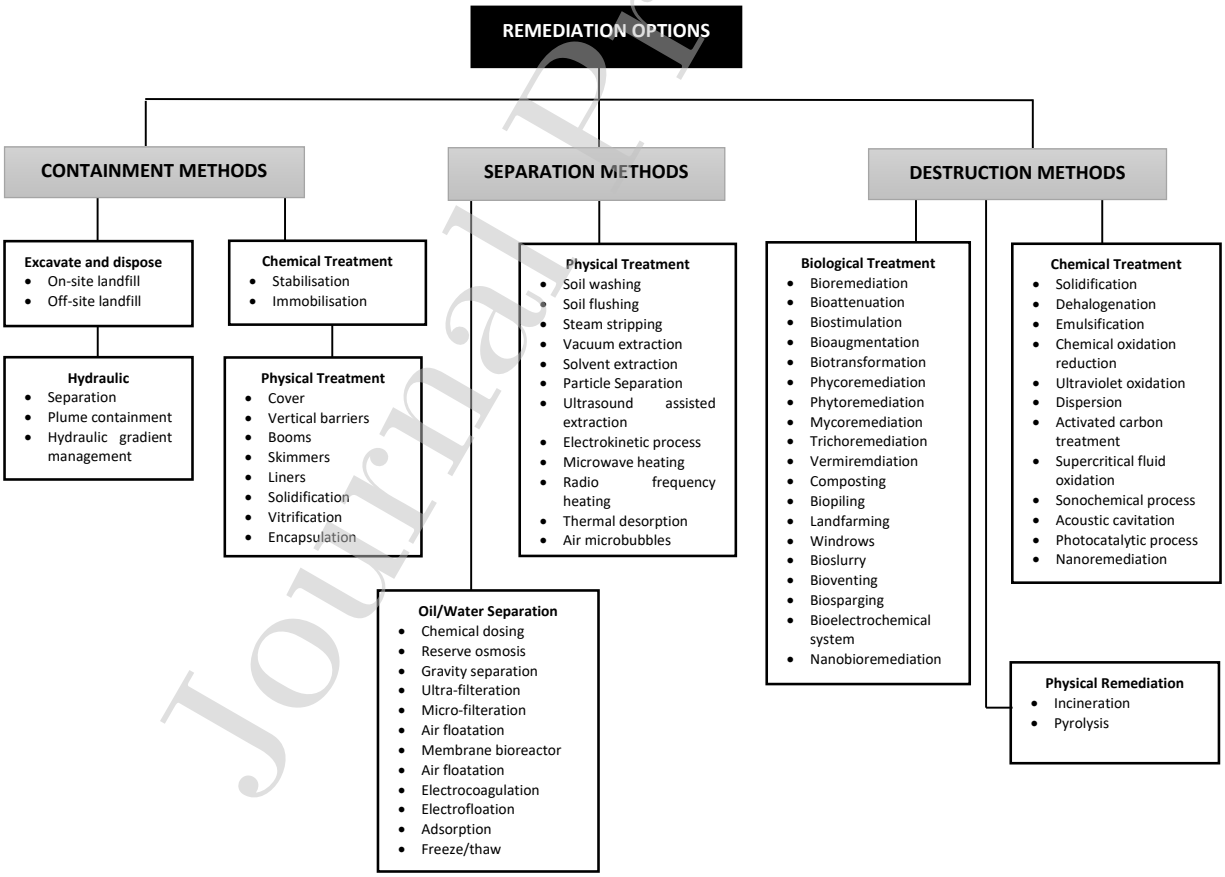


Figure 3 **Chemical process in petroleum hydrocarbon degradation**



Journal Pre-proof

Figure 4 **Remediation options for containment, separation and destruction of petroleum hydrocarbons in polluted environments**

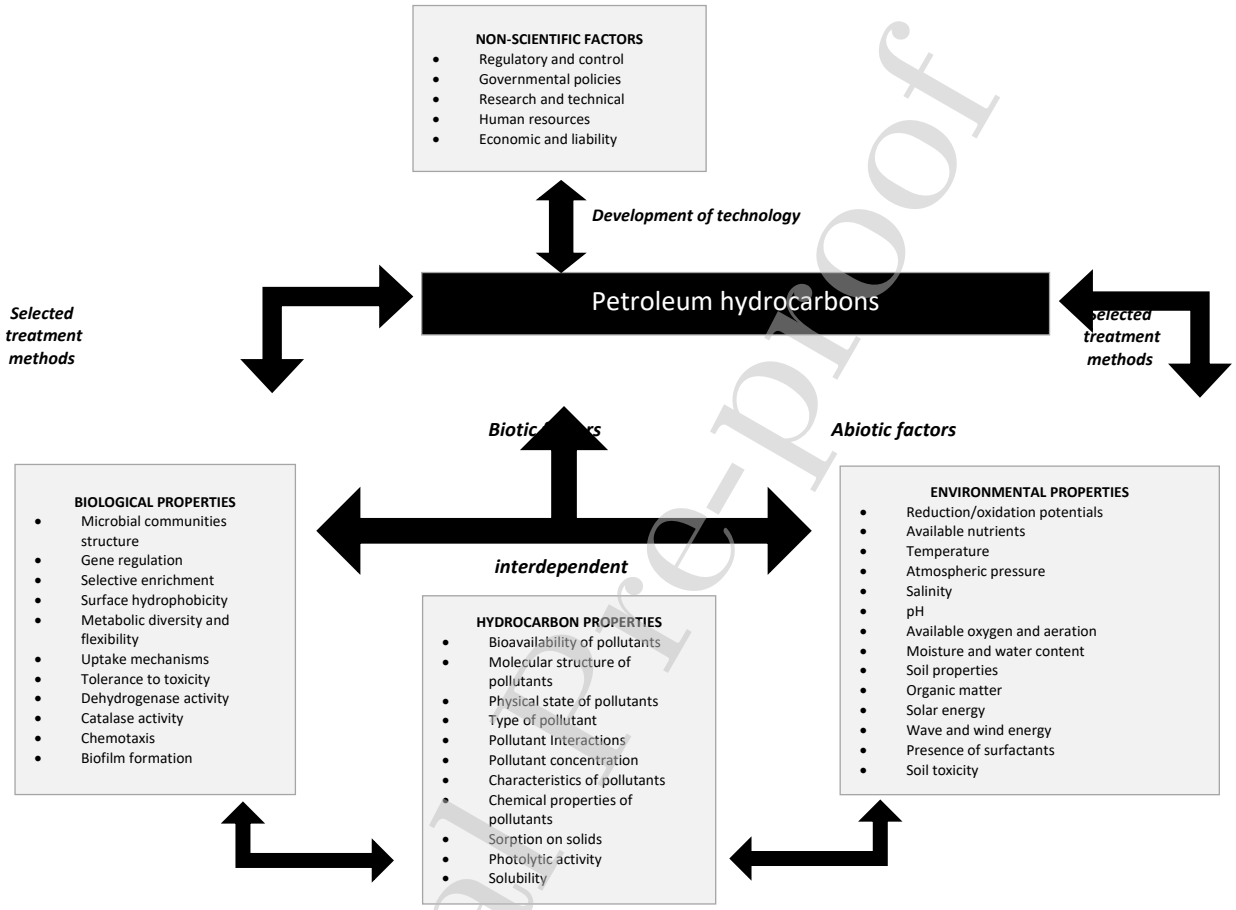
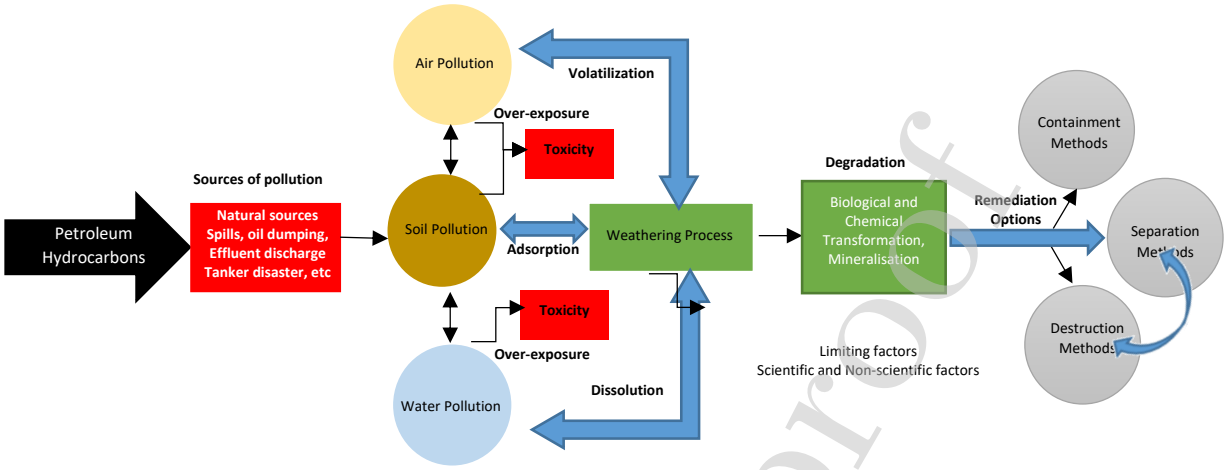


Figure 4 **Factors affecting remediation of petroleum hydrocarbons**

Journal Pre-proof

Graphical Abstract



Journal Pre-proof

Journal Pre-proof

Highlights

- Petroleum hydrocarbon pollutants in the environments cause huge ecological impacts
- The pollutants are usually introduced anthropogenically into the ecosystem
- In the soil, petroleum hydrocarbons affect soil physical characteristics
- The degradation depends on the nature, composition, physical & chemical properties
- The degradation involves biotic and abiotic chemical transformations

Journal Pre-proof

Journal Pre-proof

Conflict of Interests

The authors hereby declare that there is no conflict of interests regarding the publication of this review paper.

Journal Pre-proof